Electrochemical Impedance Spectroscopy
Prof. S. Ramanathan
Department of Chemical Engineering
Indian Institute of Technology- Madras

Lecture – 26
E- EAR Reaction, Negative Resistance (2 of 2)

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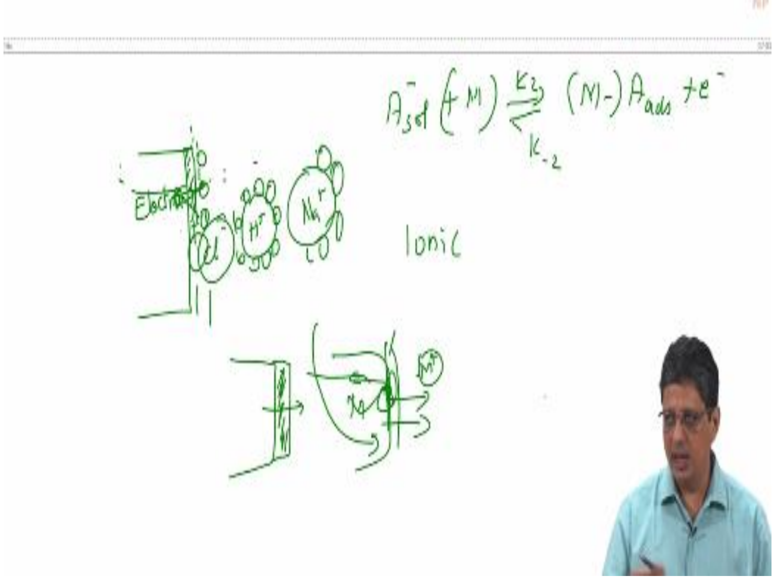

~~So~~I want to describe a little more detail of what happens when you have a reaction, electrochemical reaction. Let us say this is the electrode you have water molecules here, dipoles, we have ions here may be Cl^- ion, H^+ ion meaning it is surrounded by water molecules, ~~of course~~ other ions with water dipoles and they are lined up. Very near the electrode they are lined up sometimes this can strongly adsorb and be present.

So, that is one situation where we said, I have put the +M and M bond in the brackets to say that sometimes we explicitly mention that sometimes, we just do not write that we just write A^-_{sol} becomes A_{ads} but really means that the metal is participating in that, that is on the metal and it adsorbs. ~~and that~~ There was a question that it is going to cause a resistance so it should work like a resistance when you increase the voltage current has to increase.

See the conduction within the electrolyte that happens by ionic conduction, that means ions have to move here it can be H^+ Cl^- anyone of those ions all of them does not know the matter they move. Electrons are transferred only from this metal to that area and electrons can get transferred at this location but in the solution and independent electron will not move this solution is not an electronic conductor.

If it is a liquid metal electron can go through that electronic conductor but that is not an electrolyte, we are considering only ionic liquid here; ~~ionic liquids,~~ it can be salt dissolved in water acid or base in water mostly we are looking at aqueous or water based solutions but even in other cases in electrochemistry we normally look at ionic conductors in the liquid phase and electronic conductors in the solid phase.

So, it does not look at situations where you have a film formed on the surface that offers a resistance and then electron goes through that and it continues to go inside as an electronic conductor here in that case we can say this offers a resistance, it can increase the resistance of the system that is okay. But we are looking at cases where an ion comes here and picks up an electron or gives an electron that is a possibility. Or there is a metal, and the metal can lose an electron can become ion and the ion crosses over the double layer and then goes into the solution. First the ion that goes here electron goes into this or electron can come from here, M^+ ion can come here, M^+ ion can come and adsorb on the surface and then the electron can neutralize it and form a metal. So an independent electron does not move from metal in to the solution or from the solution into the metal independent electron is not really present in the solution that is probably answering your question but then a little later~~, okay we will take it up later then~~.

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Previous class

- RMA
  - Electron transfer + Electro Adsorption Reaction (E-EAR)

Today

- RMA
  - E-EAR (continued)
  - Reactions with two adsorbed intermediates
  - Catalytic Mechanism

So, we will continue with the derivation of the impedance expression.

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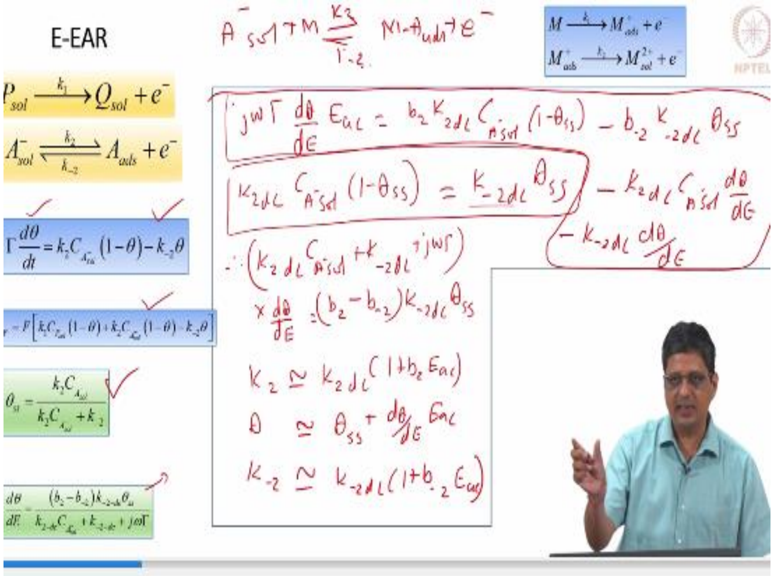

E-EAR

$P_{sol} \xrightarrow{k_1} Q_{sol} + e^-$

$A^-_{sol} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A_{ads} + e^-$

$\Gamma \frac{d\theta}{dt} = k_2 C_{A^-_{sol}} (1-\theta) - k_{-2}\theta$

$-F\left[k_1 C_{P_{sol}} (1-\theta) + k_2 C_{A^-_{sol}} (1-\theta) - k_{-2}\theta\right]$

$\theta_{ss} = \frac{k_2 C_{A_{sol}}}{k_2 C_{A_{sol}} + k_{-2}}$

$\frac{d\theta}{dE} = \frac{(b_2 - b_{-2}) k_{-2dc}\theta_{ss}}{k_{2dc} C_{A_{sol}} + k_{-2dc} + j\omega\Gamma}$

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

$M^+_{ads} \xrightarrow{k_2} M^{2+}_{sol} + e^-$

$A^-_{sol} + M \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M\text{-}A_{ads} + e^-$

$j\omega\Gamma \frac{d\theta}{dE} E_{ac} = b_2 K_{2dc} C_{A^-sol} (1-\theta_{ss}) - b_{-2} K_{-2dc} \theta_{ss}$

$K_{2dc} C_{A^-sol} (1-\theta_{ss}) = K_{-2dc} \theta_{ss}$ $- K_{2dc} C_{A^-sol} \frac{d\theta}{dE}$ $- K_{-2dc} \frac{d\theta}{dE}$

$\therefore \left(K_{2dc} C_{A^-sol} + K_{-2dc} + j\omega\Gamma\right) \times \frac{d\theta}{dE} = (b_2 - b_{-2}) K_{-2dc} \theta_{ss}$

$K_2 \simeq K_{2dc}(1 + b_2 E_{ac})$

$\theta \simeq \theta_{ss} + \frac{d\theta}{dE} E_{ac}$

$K_{-2} \simeq K_{-2dc}(1 + b_{-2} E_{ac})$

For this so we have taken up a reaction which is electron transfer reaction and the adsorption reaction, and we have written the mass balance equation charge balance equation. We can get this steady state θ value, and we are supposed to derive this and get this so look at this you can take this equation expand it and truncate it after the first term and I am going to write this and we had done this before. So I would assume that given enough time you can show that Γdθ/dT when we apply a sinusoidal potential would give rise to jω Γgamma dθ/ dE. dE/dt term has given rise to this, so this is the expression on the left side, on the right side we can expand remove the terms which are E_{ac}^2 and higher order and then we can show that under DC conditions we are going to have $k_{2dc}\,C_{A^-sol}$ $(1 - \theta_{ss})$ is going to be equal to $k_{-2dc}\,\theta_{ss}$ because we would have set this to zero under dc condition.

So, that is how we have derived θ_{ss} so this expression holds true, and therefore on the right hand side we would get terms like this $b_2k_{2dc}C_{A^-sol}$ $(1 - \theta_{ss})$– $(b_{-2}\ k_{-2dc}\ \theta_{ss})$ – $(k_{2dc}C_{A^--sol}d\theta/dE)$ – $(k_{-2dc}d\theta/dE)$ so instead of trusting that what I have written is correct. I would actually like you to try this and get this. [Please refer the video 7.13]So what you should do is first step is to write k_2 as approximately equal to $k_{2dc}(1+b_2\ E_{ac})$. θ is approximately = θ_{ss}+$d\theta$ /dE multiplied by $E_{ac.}$ k_{-2} is roughly equal to k_{-2dc} $(1+b_{-2}E_{ac})$ so what we need to do is to substitute for k_2 , θ and k_{-2} in that equation this equation right hand side. Left hand side we have written it right hand side we should substitute this and then multiply the terms there then recognize that $k_{2dc}\ C_{Asol}$ $(1 - \theta_{ss}) = k_{-2dc}\ \theta_{ss}$ that means some terms will go away. Some terms we are going to ~~throw~~remove ~~away~~ saying E_{ac}^2 is not significant and then the remaining terms are going to give you this that is my claim. Once the remaining terms are written down correctly you can rearrange it is a matter of just arranging them in Algebraic manipulation.

“Professor – student conversation starts” Sir what is the exact use of θ ss why we are calculating θ ss?

See basically if it gives you a kinetic parameters I would like you to be able to predict the impedance spectrum at a given dc potential. So now the current depends on the rate constant it also depends on fractional surface coverage which is θ. Now on top of a dc potential we are applying an ac potential because of that the rate constant will modulate will increase and decrease.

They will have certain value, on top of that value hey will show a slight increase and decrease because we are applying a small amplitude similarly the surface coverage is also not going to remain the same. See what happens is in this reaction, it does not show up very well here so I will write it here A^-_{sol} + metal gives us k_2, k_{-2}. When potential changes k_2 will change k_{-2} also changes.

Now k_2 in this case is going to increase when the potential increases k_{-2} decreases so the change is not the same it is in fact in the opposite direction. So what would happen to M_{ads}, it is not going to remain constant when I apply an ac it is going to show an oscillation it is going to increase and decrease the fractional surface coverage. Let us make up a number and say if I apply certain dc potential, 0.2 voltage with respect to equilibrium then I have 30% surface coverage. Now when I apply an ac it is going to oscillate may be between 31 to 29%, so I need to know this value so I can tell the current is going to change from so many mA/cm^2. It is going to oscillate around the dc but this is how it is going to oscillate and this is going to be the amplitude and we also see the θ_{ss} will not be in phase with the potential.

That means when I start here, so, when I look from this side let us say this is zero potential goes up comes down and goes like this fractional surface coverage under steady periodic conditions. That means initially there is going to be some transient and after that it is going to oscillate with the same period and it is going to be periodic meaning, whatever point I find here after 1 period I will find the same point here initially it is not going to be like that, there will be short time when there is a transient.

Now the θ will oscillate with respect to time current will also oscillate with respect to time however let me see if I can move to the other one. **"Professor – student conversation ends"**

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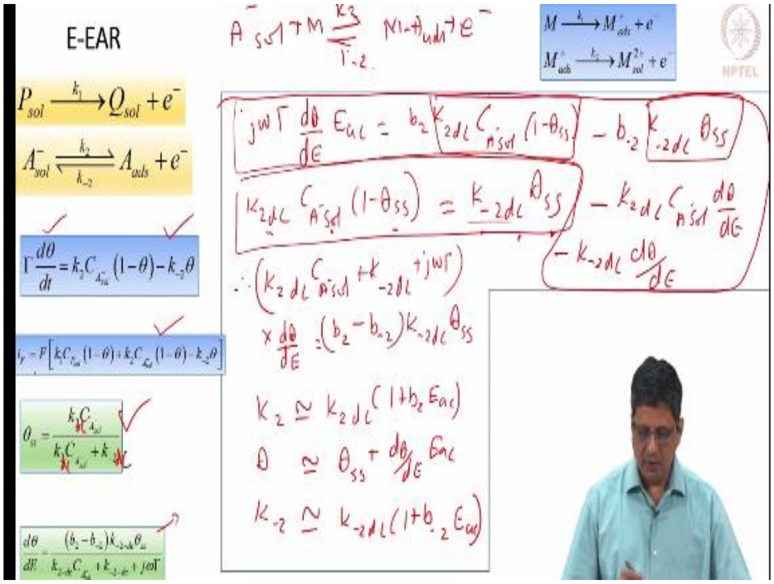

E-EAR

$P_{sol} \xrightarrow{k_1} Q_{sol} + e^-$

$A^-_{sol} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A_{ads} + e^-$

$\Gamma \frac{d\theta}{dt} = k_2 C_{A^-_{sol}}(1-\theta) - k_{-2}\theta$

$i_F = F\left[k_1 C_{P_{sol}}(1-\theta) + k_2 C_{A^-_{sol}}(1-\theta) - k_{-2}\theta\right]$

$\theta_{ss} = \frac{k_2 C_{A^-_{sol}}}{k_2 C_{A^-_{sol}} + k_{-2}}$

$\frac{d\theta}{dE} = \frac{(b_2 - b_{-2}) k_{-2,dc}\theta_{ss}}{k_{2,dc} C_{A^-_{sol}} + k_{-2,dc} + j\omega\Gamma}$

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

$M^+_{ads} \xrightarrow{k_2} M^{2+}_{sol} + e^-$

$A^-_{sol} + M \underset{k_{-2}}{\overset{k_3}{\rightleftharpoons}} M\text{-}A_{ads} + e^-$

$$j\omega\Gamma \frac{d\theta}{dE} E_{ac} = b_2 k_{2dc} C_{A^-_{sol}}(1-\theta_{ss}) - b_{-2} k_{-2dc}\theta_{ss}$$

$$k_{2dc} C_{A^-_{sol}}(1-\theta_{ss}) = k_{-2dc}\theta_{ss} - k_{2dc} C_{A^-_{sol}}\frac{d\theta}{dE} - k_{-2dc}\frac{d\theta}{dE}$$

$$\therefore \left(k_{2dc} C_{A^-_{sol}} + k_{-2dc} + j\omega\Gamma\right) \times \frac{d\theta}{dE} = (b_2 - b_{-2}) k_{-2dc}\theta_{ss}$$

$$k_2 \simeq k_{2dc}(1 + b_2 E_{ac})$$

$$\theta \simeq \theta_{ss} + \frac{d\theta}{dE} E_{ac}$$

$$k_{-2} \simeq k_{-2dc}(1 + b_{-2} E_{ac})$$

However let us say we have given the ac potential some time ago, and by this time they are going to say, this is when we start measuring t = 0 by this time it has come to steady periodic value for the current and θ everything, so the potential goes like this the current will not necessarily go with the same phase if it goes to the same place this is how it look like.

Current may also show a phase difference. θ will usually show a phase difference unless the parameter values are aligned such that whenever one rate constant increases the other rate constants also move in such a way that the fractional surface coverage does not change. So what happens in those cases is θ is also going to have a phase difference. If there is no phase difference all of them at time t = 0 they will start at this location. If there is no phase difference it is going to go like this if there is 90 ° phase difference it is going to go like this or it going to be +90 °, -90 ° depending on that it is going to show us shift and this θ value is a starting or where is average θ value is not zero, it is some value. We are writing in terms of θ ss because at the dc we can measure not we can measure we can calculate the k_{1dc} k_{2dc} and k_{-2dc}. We can calculate θ_{ss} we can calculate the current at the dc this ac current depends on θ ss depends on the $k_{1dc,}$ k_{2dc} and the exponents b_1 b_2 etc and of course it also depends on ω. So what else can we write it off θ_{ss} is an intermediate variable for us, and it has a physical meaning θ_{ss} is written in terms of ~~k_1 k_2~~ k_{1dc} k_{2dc} k_{2dc} k_{-2dc} here and in terms of C_{A^-sol}.

“Professor – student conversation starts” “θ is a term dependent on k_2 and k_{-2} right?” “k_2, k_{-2} C_{Asol}yes this is in this particular example in another example another mechanism. It is going to depend on certain variables, depending on what the mechanism is. Because we can assign the physical meaning to θ here we would like to represent in terms of θ. Otherwise they can rate everything in terms of k_1, k_2, k_{-2}, C_{A^-sol}, C_{P^-sol} just what is convenient to us”. **“Professor – student conversation ends”**

But are you able to get, are you able to expand it and get it? Some of you, yes okay so the calculations are done. We would get dθ /dE and I can simplify some of the terms I recognize k_{2dc} $C_{A^-sol}(1- \theta_{ss})$ is same as k_{-2dc} θ_{ss}. Therefore on this side I can take this term, and make it substitute with this term so it simplifies it a little bit. Otherwise it does not matter if you are going to use the program to calculate this, you can use this way you can use the original expression? You would get the same number anyway. When you write it you want it to look at fewer terms, it looks better than you can write like this so dθ /dE is necessary because when we expand I_F in Taylor series and then truncate it we would get certain items.

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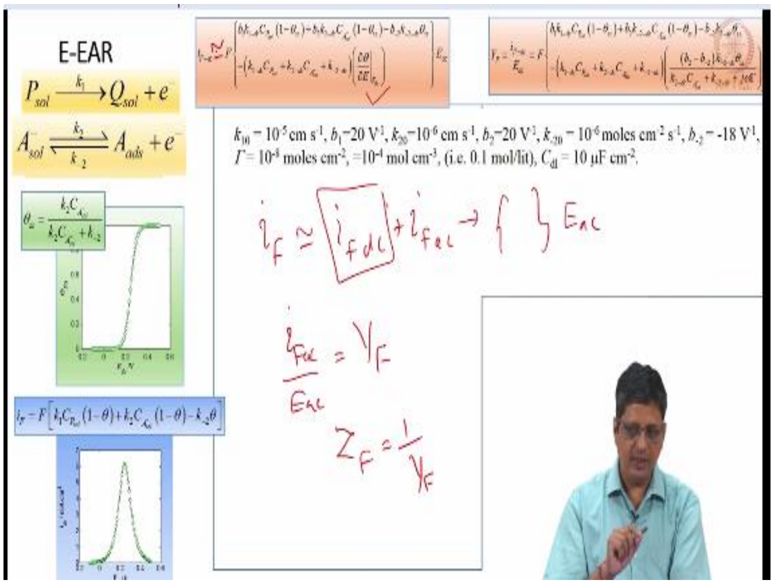

E-EAR

$P_{sol} \xrightarrow{k_1} Q_{sol} + e^-$

$A^-_{sol} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A_{ads} + e^-$

$\theta_{ss} = \frac{k_2 C_{A_{sol}}}{k_2 C_{A_{sol}} + k_{-2}}$

$i_F = F\left[k_1 C_{P_{sol}}(1-\theta) + k_2 C_{A_{sol}}(1-\theta) - k_{-2}\theta\right]$

$k_{10} = 10^{-5}$ cm s^{-1}, $b_1 = 20$ V^{-1}, $k_{20} = 10^{-6}$ cm s^{-1}, $b_2 = 20$ V^{-1}, $k_{-20} = 10^{-6}$ moles cm^{-2} s^{-1}, $b_{-2} = -18$ V^{-1}, $\Gamma = 10^{-8}$ moles cm^{-2}, $= 10^{-4}$ mol cm^{-3}, (i.e. 0.1 mol/lit), $C_{dl} = 10$ µF cm^{-2}.

$i_F \simeq \boxed{i_{Fdc}} + i_{Fac} \rightarrow \{\ \} E_{ac}$

$\frac{i_{Fac}}{E_{ac}} = Y_F$

$Z_F = \frac{1}{Y_F}$

When we extend I_F and approximately right this we can write this in terms of all the parameters that this is $I_{F\text{-}ac}$. We have done the expansion for I_F yesterday, we had written it as $I_{F\text{-}dc} + I_{F\text{-}ac}$ where $I_{F\text{-}ac}$ is the term that comes in terms of E_{ac}. E_{ac}^2 and other terms are neglected anything that does not depend on E_{ac} which is just a constant that happens to be the dc component. So within the bracket you see an expression for dθ /dE.

And in order to calculate it, we had to use the mass balance equation and get that expression again this just needs us to expand k values k_1, k_2, k_{-2} in Taylors series and truncate it after the first E_{ac} it requires to expand θ in terms of θ_{ss} + (dθ/dE) E_{ac} truncate it at that level, take the product rearrange and simplify everything, you would get everything but you would get d θ/dE we need to substitute for dθ/dE.

Once you do that you get i_F in terms of E_{ac} take the ratio of $I_{F\text{-}ac}$ to E_{ac} and what you get is the faraday admittance. Take the inverse to get the faradaic impedance. Point to note here is it depends on ω. That means when I vary frequency, I will get a change with respect to the frequency, I will get a change in the current for the same potential change, I will get change in the current that basically means the impedance cannot be represented by a simple resistance.

It needs in this particular case it needs a Maxwell element with the capacitor. Now, I think we also saw that θ_{ss} will show an s shaped curve it will show a very low potential going to go to zero and very high potential it is going go to one. The current values here I mean the dc current value i_{dc} as a function of E_{dc}. We do not need faradaic impedance expression for that all that we need was this at dc.

You can calculate the k_1, k_2, k_{-2} you do not need the gamma value, you need k_{10}, b_1, k_{20}, b_2, k_{-2}, b_0, b_{-2}, double layer capacitance is not necessary.

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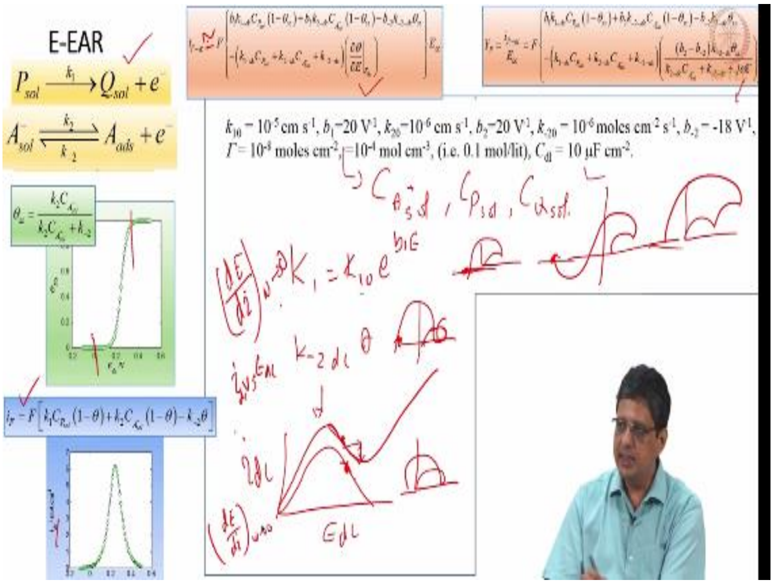

E-EAR

$$P_{sol} \xrightarrow{k_1} Q_{sol} + e^-$$

$$A^-_{sol} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A_{ads} + e^-$$

$$\theta_{ss} = \frac{k_2 C_{A_{sol}}}{k_2 C_{A_{sol}} + k_{-2}}$$

$$i_F = F\left[k_1 C_{P_{sol}}(1-\theta) + k_2 C_{A_{sol}}(1-\theta) - k_{-2}\theta\right]$$

$k_{10} = 10^{-5}$ cm s^{-1}, $b_1 = 20$ V^{-1}, $k_{20} = 10^{-6}$ cm s^{-1}, $b_2 = 20$ V^{-1}, $k_{-20} = 10^{-6}$ moles cm^{-2} s^{-1}, $b_{-2} = -18$ V^{-1}, $\Gamma = 10^{-8}$ moles cm^{-2}, $c = 10^{-4}$ mol cm^{-3}, (i.e. 0.1 mol/lit), $C_{dl} = 10$ µF cm^{-2}.

$C_{A^-_{sol}}$, $C_{P_{sol}}$, $C_{Q_{sol}}$

$\left(\frac{dE}{dt}\right)_{\nu \to 0}$ $k_1 = k_{10} e^{b_1 E}$

$k_{-2dc}\,\theta$

i_{dc} vs E_{dc}

i_{dc}

$\left(\frac{dE}{dt}\right)_{\nu \to 0}$

E_{dc}

(Please refer video 18.20) This is supposed to be I think C_{-sol} C_{Psol} and C_{Psol} concentration. This is one example you can take other kinetic parameter and see if the system is little different or the concentration is different what you would see this case dc current goes up and comes down. Physically what it means is that as dc potential is very low reaction happens at the very low rate. P does not become Q unless the dc potential is significant.

This is driven only when potential is positive this reaction will happen to a large extent. When the potential is zero or negative, k_1 becomes if E is zero it is just k_{10} if E is negative it is going to decrease when E is positive it is going to be increasing. So k_1 becomes very small number. Therefore, first reaction will not happen to a significant level when you go through low potentials k_2 also become small number.

When the potential is small θ becomes close to zero. Now this reverse rate is going to be k_{-2dc} multiplied by θ. k_{-2} will increase whenever the potential goes down but θ becomes zero therefore the reverse reaction rate is also very low. So what happens is when you go to very low potential the rate is low, rate of each reaction is low and each reaction is an electro chemical reaction but since each reaction is not significant is not happening to a significant extent, we get net current as close to zero. When the potential is very high, the surface is fully covered with adsorb species that means the first reaction will not happen to a significant extent even though the rate constant is high there is no bare surface exposed. Because there is no bare surface the second reaction forward reaction also cannot happen it requests the bare surface reverse reaction in the second reaction the rate constant is low although the concentration of a adsorbs is high. So put together this tells us that the current is going to be very low when you go to very high potential. The reason the current is more or less zero is different at low potential is zero, at large potential it is zero but for different reasons in one case the surface is bare and in another case the surface is fully covered with an adsorbed species, but in both cases currently is going to be very close to zero.

In between when surface is partially covered, with adsorbed species and the constant values are not close to zero it is moderate. Then you would get a positive current it goes through this and decreases and come down. So, if you take polarization curve current verses potential let us say it shows something like this. It may show something like this and it may show something like this does not matter. If you take an impedance spectrum in the region where it shows a negative slope, when it shows a negative slope it means around this region when they increase the potential current will decrease. When that happens the impedance spectrum at low frequencies will show a negative value. It usually starts like this after that it may do this, it may do this, it may go like this it would settle on the real axis. We have got data where it goes like this, we have seen data with a variety of patterns, but if you go too low enough frequency it will always settle at the negative axis. As long as the slope is negative.

Why do we need to go to low frequency? This is taken at dc if I go to high frequency the capacitive current will contribute to that and this expression comes to negative value only when ω is close to zero. This is taken at dc meaning, I take potential here I get the current value I go to this potential take the current value. if I go to that potential and slightly move that is equal going at zero frequency or low frequency.

If I move rapidly this potential dynamic polarization curve does not tell me what will happen that is why we need impedance spectrum at this potential. This curve tells us what would happen if you are more or less at zero frequency. Impedance spectrum low frequency data tells us dE/ di value when ω is tending towards zero or low enough value so the relationship between current potential diagram and impedance curve is.

This is current potential diagram, this is impedance curve. That is current potential diagram gives you i_{dc} verses E_{dc} impedance spectrum gives you dE/di which is going to be the inverse of the slope of this impedance spectrum at ω tending to zero is going to be equal to the slope of that potential dynamic polarization.. **"Professor – student conversation starts**" In "Y_F equation except the ω nothing else is dependent on E_{ac}, in Y_F impedance".

"Y_F does not depend on E_{ac}, ω also does not depend on E_{ac}, ω is what we applied the frequency, okay, what we apply. Y_F is the ratio of I_F to E_{ac}"and "I am just asking you in plots we would not get any in Eac right in plot with respect to dc". "You mean in the impedance spectrum or you mean in polarization current verses potential".

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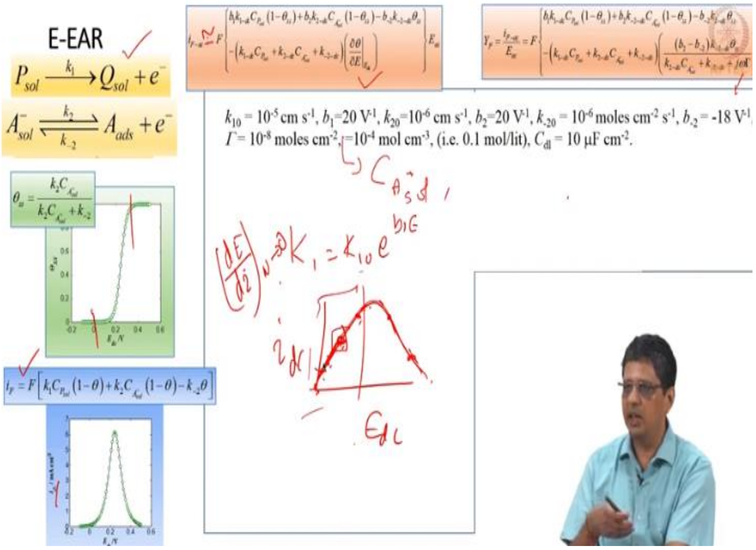

E-EAR

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$k_{10} = 10^{-5}$ cm s^{-1}, b_1=20 V^{-1}, k_{20}=10^{-6} cm s^{-1}, b_2=20 V^{-1}, k_{-20} = 10^{-6} moles cm^{-2} s^{-1}, b_{-2} = -18 V^{-1}, Γ = 10^{-8} moles cm^{-2}, =10^{-4} mol cm^{-3}, (i.e. 0.1 mol/lit), C_{dl} = 10 μF cm^{-2}.

The experiment is conducted like this: ideally you would go to potential wait there monitor the current, when it stabilizes note the current, go to the next potential wait for some time monitor the current when it stabilizes note that current, and then we generate the curve. Practically what happens is we start at a potential scan it at a slow enough rate and monitor the current. The assumption is it is going very slowly we consider it to be more or less at a steady state condition. It is like taking the picture move there stand take a picture move that stand take a picture okay that is the theory. What we do is walk slowly and keep clicking and we think it is going to be more or less similar, where as an experimental cyclic voltammetry usually will be like riding in a motor cycle or going in a car and taking picture. That is probably not going to represent the stationary position. But practically this what you would end up doing most of the time, if you really want you can do this in case of going there and waiting and getting the current value and recording that. So that is how the dc value is obtained. To obtain impedance spectrum is you go to some dc potential it can be at equilibrium, it can be some other potential wait for some time it will stabilize. Wait for some time it will stabilize and apply an AC on top of the dc. Again you have to wait for a short time to stabilize typically short time depends on the system and then take later the software will allow you to wait for certain time or certain number of loops and then take that. Usually commercial software allow you to do that. So, impedance spectrum means information just at this point around that point at many many frequencies, around this point at many many frequencies around this point at many may frequencies this so if we take impedance spectrum at multiple potential you would get lot more information that taking DC current DC potential. On the other hand if I take impedance spectrum only, at this frequency I mean only at that DC potential, I am not going to get information on how this is going to behave with other DC potentials. So you should take polarization curve ideally you should have impedance at spectrum at every DC potential but that is not going to be happening at a few DC potential planning at this range of interest. If a range interest is limited to this early you probably want to take 3, 4, 5 whatever number it depends on again there is not much point in taking impedance spectrum around this because if the 5 or 10 mV amplitude overlaps with the next point you are probably not really getting a lot more information if this range is 300 mV I can take the impedance spectrum I will take that input and spectrum. If this range is 20 mV. I probably would not bother taking like 5 spectrum of 5 different dc potentials. But this is more of a practical aspect but does that answer your question? "Yeah that is what for a given DC potential if we change ω iac also we will change right".

"I_{ac} will change, yes that is how we get the impedance spectrum otherwise if it does not change well say representative of a resistance, at least they have a double layer capacitance. So, you will have a change in current, you will have a change in impedance. Yes shall we proceed ?"
"Professor – student conversation ends"
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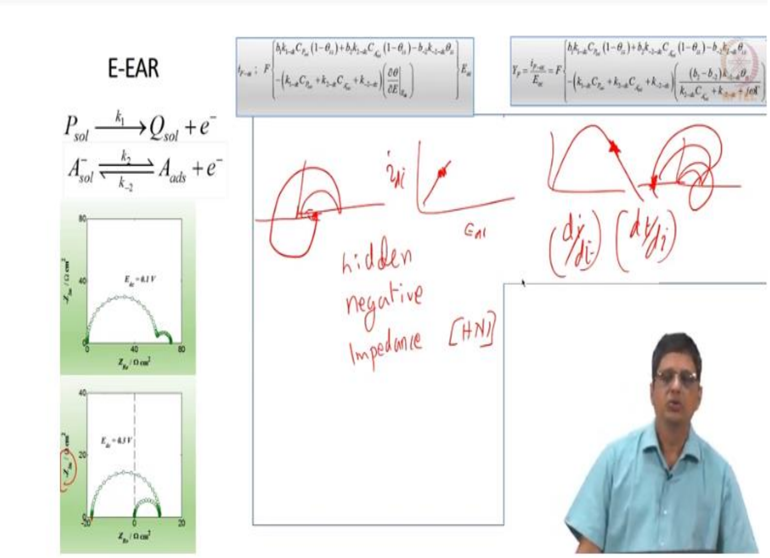
E-EAR

$P_{sol} \xrightarrow{k_1} Q_{sol} + e^-$

$A^-_{sol} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A_{ads} + e^-$

So, we can write the expression for this and for a set of kinetic parameters which are given in the earlier slide. You can show that this is how the this is how the patterns will come in the complex plane representation, right?-Imaginary of impedance and the positive real value of this impedance. So, it basically the points are more and more dense here, which means its settling there as you go further down in frequency, it will just stay here.

(Please refere to the video 29.01) Of course it is a noise free data it is synthetic data, okay, when you measure there will be some noise. But usually if the system is good you would see it settling ~~that~~here. Sometimes you will see data where it goes like this comes here comes like this. Here if you look at the I_{dc} versus E_{dc} wherever this is taken, that would be a positive number that slope is a positive number, that means finally it should settle on the right side.

(Please refere to the video 29.35) So, by looking at the current-potential diagram, if the current potential diagram looks like this and you take impedance spectrum at this location even before taking the impedance spectrum, you can tell I expect the impedance spectrum to settle somehow maybe like this maybe like this. Somewhere it has to settle on the negative axis, and if the experiment is done correctly I know the slope value it should settle around that point.

It should settle at that point exactly but experimentally there is going to be some noise. So around this point I know the slope so the di/dE is known to me, so I can calculate the dE/di and that is where this number is going to be. Look at this curve, you cannot tell that the impedance will have negative values at the real value. So this type of impedance is called hidden negative impedance, meaning looking at the polarization curve you cannot tell that this impedance curve will go through that left plane in the complex plane. Those are not very common though, if time permits I will create an example and show you one, right now I just want you to be aware of it, that if the polarization curve shows a negative slope you should expect the low frequency values to settle at the negative real axis. If the polarization curve shows a positive slope you should expect it to settle at the positive real axis and the inverse of the slope should match with the point at which it settles with an experimental error. So ~~this~~it is possible to do some consistency checks it is necessary to do consistency checks if you get impedance spectrum we should do KKT validation, that is for that spectrum alone. When we get multiple impedance spectra at various dc potentials and you have dc current and dc potential you should get that anyway, when you the experiments.

Taken at slow scan rate then you should check whether the polarization resistance that you get here is matching with the inverse of the slope that you get. So, you have confidence in the data when the internal consistency checks show that there is a good match.

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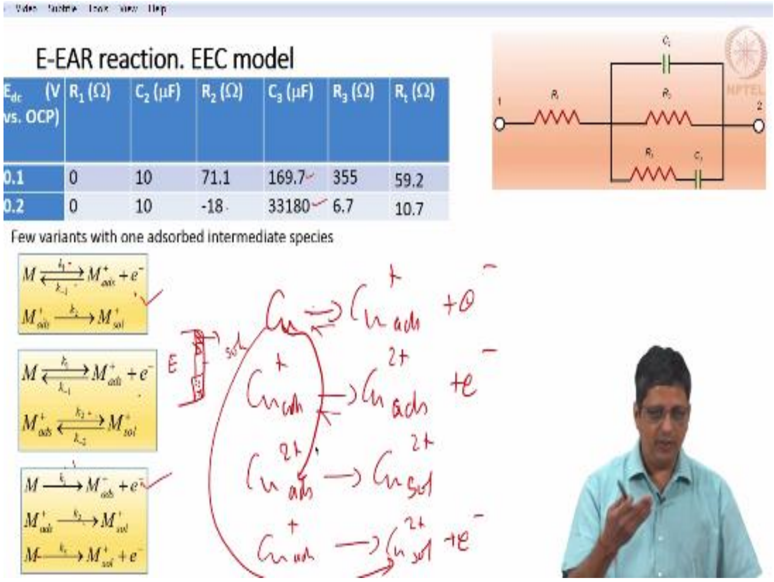

E-EAR reaction. EEC model

E_{dc} (V vs. OCP)	R_1 (Ω)	C_2 (μF)	R_2 (Ω)	C_3 (μF)	R_3 (Ω)	R_t (Ω)
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0.2	0	10	-18	33180	6.7	10.7

Few variants with one adsorbed intermediate species

$M \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} M^+_{ads} + e^-$
$M^+_{ads} \xrightarrow{k_2} M^+_{sol}$

$M \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} M^+_{ads} + e^-$
$M^+_{ads} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} M^+_{sol}$

$M \xrightarrow{k_1} M^+_{ads} + e^-$
$M^+_{ads} \xrightarrow{k_2} M^+_{sol}$
$M \xrightarrow{k_3} M^+_{sol} + e^-$

Now I can model those data using this circuit, except that I have to allow negative values for the R_2 here. This particular value shown for the firstst spectrum which goes like this all the elements are positive for the second spectrum which goes like this, one of the elements is negative you also see that there is a large capacitance value. It is just to show you that when you model this spectrum with the EEC you will get values, R_2 is negative.

C_3 is very large value it is not easy to get 33 mF in a real capacitor. You can get it is not that you cannot get it but in the electrochemical system we do not have to imagine there is a negative resistance we do not imagine that there is going to be a capacitor or an inductor. Without resorting to any of those just by saying this is the reaction, and this is the adsorbed species when a modulate the voltage when you modulate the potential this happens to modulate like this what happens is when they increase the potential surface coverage becomes more when I decrease the potential surface coverage of this adsorbed species becomes less. When I do it at a very slow scan rate, very slow frequency, when the surface coverage becomes more the net current actually becomes less in this range. [Please refer to the video 33.28] So, when I go ~~to~~ from here to here up to some level, when I increase potential surface coverage becomes more current also becomes more. So it is in the positive region. From here to here when I increase the potential surface coverage becomes more and because surface coverage becomes more this reaction slows down, the vacant state becomes less current becomes less. Because of that when I increase the potential, current decreases.

So, it appears as a negative resistance because I am taking dE/di, I am not looking at E/i is still positive here. This is the E value this is the i value that is still positive but the slope which is dE/di is negative here, so I get negative impedance. I can explain by physical processes rather than thinking there is some negative resistance there is some inductance it means of the adsorbed species, if you have a capacitance you can explain it with adsorbed species.

If you have inductance, same adsorbed species with different kinetic parameter value can give it or even the same kinetic parameter value at a different DC potential value can give you inductance. So same reaction conducted at one DC potential, if you take impedance at that potential can give you a capacitance another DC potential same reaction same kinetic parameter can give you inductance. So lot of times you will see people resorting to some phrases because they do not do this kind of analysis. They just look at the circuits they realize they have to model with an inductance they go to prior literature and say this inductance may arise because of something, adsorbed species interaction. If I ask what is that adsorbed species interaction it is very vague whereas it is possible to explain using proper reaction, with proper kinetic parameters, proper dependence of the parameters to the potential, when you change the potential it has to change exponentially. That is what we would expect from a normal electrochemical reaction. The rate constant still changes exponentially, it is just the rate does not change like that, because rate inverse k as well as θ in this example. ~~So~~ I am not going to derive the expressions for this but you can come up with own variants of this reaction. I can say metal goes into metal plus adsorbed. That means, there is metal it loses an electron and this surface area, this is from the side this is metal this is electrolyte. I can look at it as the front face of the metal and I can say this area, metal has lost electron therefore it is adsorbed species, considered as adsorbed species it is not coming from solution. This can pick up an electron and become a metal atom again, that is the reverse reaction. It can also go into the solution, then it will leave a vacant metal again below that.

If it goes into the solution this becomes normal metal again at the same time another metal can become metal adsorbed. The first reaction rate constants, k_1 and k_{-1} depend on potential k_2 does not depend on potential because there is no electron transfer involved. For this you should be able to write the mass balance equation charge balance equation expand the terms in Taylor series, truncate it rearrange and get an expression for impedance. You should be able to write the DC potential verses current, take some values for the kinetic parameters and simulate or show this is how the current potential will look like, this is how the impedance at a given DC will look like. You can make the reverse reaction possible for the second step. That is again not going to depend on the potential this is actually superset of the firstst example. [Please refer to the video 38.07] This is the superset of the example we have seen before originally we said M going M^+_{ads} adsorbed this is just a forward reaction that there is no reverse reaction and M_{ads} going into M^+_{sol} again. So I am creating little more complicated or a superset for this superset for this you can write this but then this means the solution already contains sufficient amount of metal + solution that is a possibility. It is well mixed, but it already contains certain amount of M^+_{sol} and that quantity is not changing when we allow to dissolve or deposit, and in all these cases we assume mass transfer is fast. We assume solution resistance is negligible if you have to take that into consideration few more complications will come, that we will see later. I also want to show another example, I want you to think about this example.

[Please refer to video 39.01] We go back to the original metal going to M_{ads}^+, releases an electron metal M_{ads}^+ adsorbed on the surface goes into the solution, we have seen this before in addition I can say this metal can become metal adsorbed its one step. Next step it goes into solution that what you have seen before I can say third metal goes directly going to solution and take our given electron here, that means it is a parallel reaction.

Metal becoming M_{ads}^+ become M_{sol}^+, of course this happens with an electron transfer. In parallel, metal can directly go and that happens at a different, rate with rate constant k_3. So, if metal becomes metal adsorbed and the surface is mostly covered with metal adsorbed then only this reaction will happen to large extent the third reaction will not happen to large extent because there is no bare metal ,do you understand?

This when it happens, it will regenerate the metal the metal that is there goes out another metal below that is exposed, whereas (when) electron is taken out it does not go out until it goes out the metal atom below that cannot lose another electron that is assumption here so this would give raise to another type of polarization curve.

"Professor - student conversation starts" "But we can assume that some part of the surface is going directly to the solution. And some parts is releasing electrons and going back". "Yes that is the mechanism three here" "But you said the surface is releasing an electron and then going in the solution then the previous back one". "Yes let us say this is metal adsorbed metal has become metal adsorbed taken an electron, before this goes into solution this metal atom will not lose an electron why it is already positive here. the neighbouring atom below that will not be allowed to lose an electron. Because this atom has already lost an electron of course you can ask the question what about these can they lose an electron by Langmuir isotherm model we say whether this is M_{ads} or neutral metal, it does not affect the rate of the other one". "I am saying that you said in that the k_3 might be negligible in case of third case." "No if the rate constants are such that at some potential mostly metal is covered with metal adsorbed. Let us say this is fast this is slow that means it is not happening at a faster rate, this is also slow compared to the k_1. Then at low potential most of the surfaces bare metal, so, this is occur to some level this will also occur to some level. When they go to high enough potential most of the surface will be covered with M_{ads} that means this surface only possibility is k_2 the second step can push it.

This will occur but to a small extent because the vacant metal site is not that much there are only few sites. Means we are assuming complete coverage it will happen only for certain values of k_{10}, b_1, k_{20}, b_2, k_{30}, b_3. I would like you to visualize the possibility, I am not saying for this mechanism all the time it is going to happen like that. This mechanism when k_{30} and b_3 are very small compared to k_1 and k_2 then this mechanism is same as pretty much the same as the mechanism with only first and second step, that is a variant. But generally unless I know the values, I cannot say this could happen like this and that could happen like that etc so I have to take normally if you get a spectrum I will see if I can explain this based on whatever prior information I have about the system. If it is copper I would say copper is going to Cu^{2+}.

But Cu^{1+} is also stable we can have salts of oxides of Cu1 so I would say copper will become Cu1. Cu1 will become Cu2 that is a possibility copper can directly become Cu2 that also a possibility, if that is able to explain and I do not see evidence for presence of Cu1 by any other technique, then that is good enough if it do some analysis like XPS. it shows that there is a Cu1 present there, Cu2 is also present then probably sensible for me to propose a model where Cu becomes Cu1, Cu1 becomes Cu2 if that explains it well and good.

[Please refer to the video 43.22] So, I can propose a mechanism like this, copper becoming Cu^+ + e^-. This is Cu^+_{ads} becoming Cu^{2+}_{ads} . I can see it goes into solution if this explains done but if I see it on the surface I should say maybe this is what they should do.

If this explains polarization curve as well as the impedance spectra well and good does not explain what can I say? I will say okay this is one this I will say Cu^+ this I will say Cu^{2+} this is vacant. I am looking it from inside this is electrode and this is solution electrode. so I am saying this Cu^+ has to become Cu^{2+} and then go into the solution, that is what our model says. You see addition to that maybe I will say directly going to solution by giving one more electron so I can say Cu^+_{ads} becoming copper$^{2+}_{sol}$ + e^- is also possible. That is going via this path or going directly, I can add one parallel path this may be reversible. This may be reversible, this depending on what I know about the solution. Does the solution have Cu^{2+} and by removing it as quickly as possible in which case the reverse reaction will not happen.

If the solution does not have Cu^{2+}, knowing this situation I can say it is reversible or I can it is not possible I have to take only the forward reaction into consideration. I can also say why should I go through all this I can say copper directly becomes Cu^{2+}_{sol} copper directly becomes directly Cu^{2+}_{ads}. These are all possibilities you want to come up with a reaction mechanism, that can explain this observed results polarization results, typically impedance results any other analysis that you do may be XPS because normally you do not know the charge on the surface unless you do XPS. But whatever other knowledge you have about this system the mechanism that you propose should account for those and explain the electro chemical results. So reason I am showing few mechanism is so that you can come up with some mechanism, propose a mechanism and you should know how to derive the impedance you should know how to derive the polarization curves with I_F values and then match with this. Optimization is next step, but first, given a mechanism given a set of parameter can you write the current can you rate the impedance expression? Next you should come up with a mechanism for your system, and then for a trial value should be able to write this. And then optimization has to be done as the next level of match. "Any change in polarization curve corresponds to reactions how polarization curve should look any difference". "You have to generate and see it is not that difficult I am hoping by know this and by next few classes you should be confident enough you should be able to tell me any mechanism as long as you guarantee me that the solution resistance is negligible and mass transfer is fast, rapid I can tell you the current I can tell you that impedance expression for any given dc, for any given parameter that is what you should be able to do at the end of this few classes. Now you should be equipped with that, at least that is my goal. **"Professor – student conversation ends"**.

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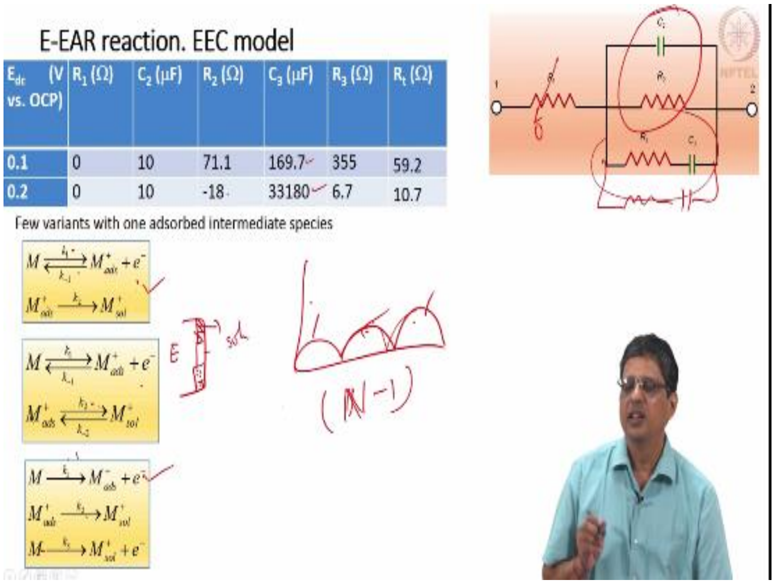

E-EAR reaction. EEC model

E_{dc} (V vs. OCP)	R_1 (Ω)	C_2 (μF)	R_2 (Ω)	C_3 (μF)	R_3 (Ω)	R_t (Ω)
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Few variants with one adsorbed intermediate species

$$M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M^{+}_{ads} + e^{-}$$
$$M^{+}_{ads} \xrightarrow{k_2} M^{+}_{sol}$$

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$$M \xrightarrow{k_1} M^{+}_{ads} + e^{-}$$
$$M^{+}_{ads} \xrightarrow{k_2} M^{+}_{sol}$$
$$M \xrightarrow{k_3} M^{+}_{sol} + e^{-}$$

Now what mechanism should you propose, we can get some hints under these conditions. [Please refer the video 47.26] If you get three loops like this, high frequency loop would come from double layer capacitance and actually not this is charge transfer resistance this is polarization but that is all right from one resistance here in parallel with the double layer capacitance. This we assume, it is negligible for now if I see two more loops I cannot model it with this alone for a circuit. I should add 1 more at least in the mechanism you need at least two intermediate species, two adsorbed intermediate species to generate two curves here, these correspond to two time constants. Time constant is RC here, out there it is going to depend on k_1 k_2 etc. But if I see N number of loops I can assign one loop to double layer capacitance, in parallel with the resistance. The remaining number of loops would correspond to remaining number of adsorbed species in the reaction, as long as the reaction is fairly simple including these reactions. In some exceptional cases it is possible that the reactions are redundant, meaning you may have ten adsorbed species but effectively may be able to give you only fewer number of loops, but I do not think we are worried about that. If you can manage two adsorbed species for now by end of this course it is good enough. With the same one of the species you can see there are many possibilities of reactions you can make, so this gives you hint on how many adsorb species are necessary.

It does not tell you what exactly is the mechanism. So in a mechanism in a system let us make up this thing.

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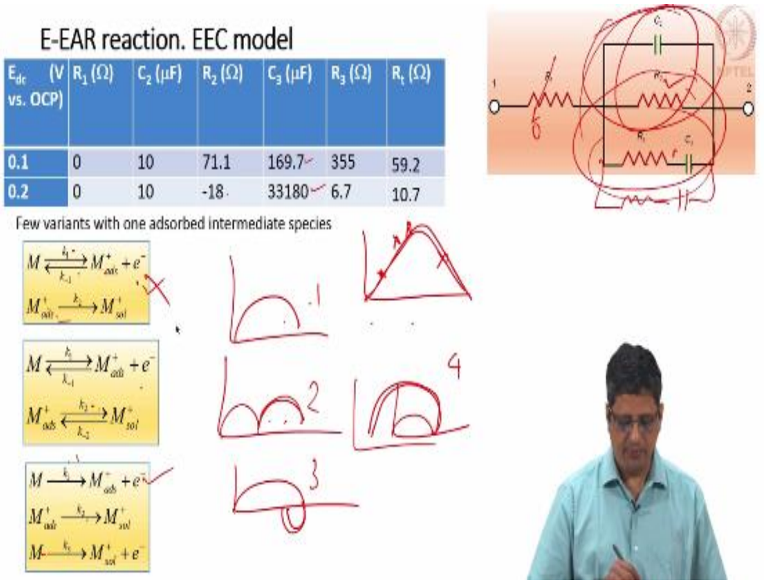

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$$M \xrightarrow{k_3} M^+_{sol} + e^-$$

[Please refer to video 49.35] I have four DC potentials at this case I have taken four spectrum. 1 2 3 and 4 th one is here, first shows the look like this. 1 2 3 4 spectra are shown here. ~~With one reaction mechanism~~ It is possible that the one reaction mechanism can be used to generate this or model this, whereas if I use circuit for one, I have to use this circuit, second I have to use this circuit, third I have to use this with negative values, fourth I have to use this with negative value for another element.

All that we see is this is one time constant, this is one time constant, this is one time constant, this can be modelled with one adsorbed species. One adsorbed species, but a simple reaction like this may not give you a curve which is going down, therefore I cannot use this mechanism. If you take many reactions and generate the curves, polarization curve as well as the impedance for a variety of parameters, you can get the feel for what mechanism can generate this data but you should know something about this system to say these intermediates are possible. You cannot just randomly make a mechanism, without substantial evidence it is not that good to do that.

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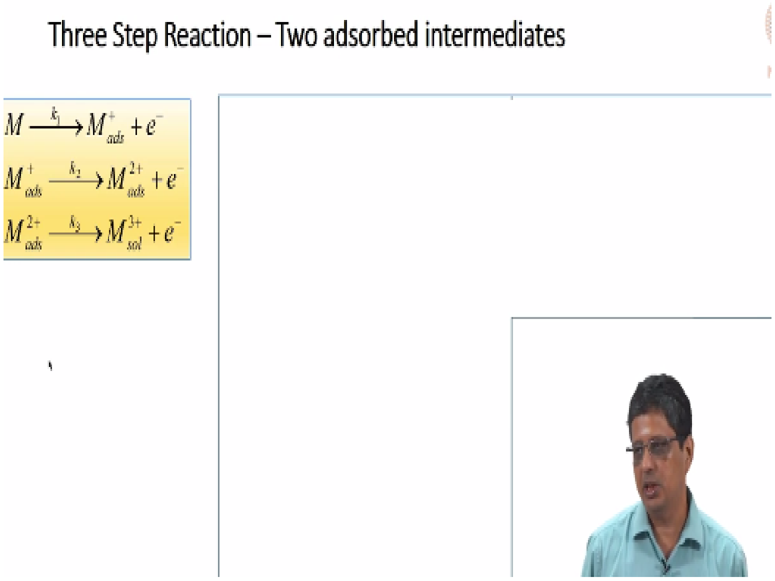

Three Step Reaction – Two adsorbed intermediates

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

$$M^{+}_{ads} \xrightarrow{k_2} M^{2+}_{ads} + e^{-}$$

$$M^{2+}_{ads} \xrightarrow{k_3} M^{3+}_{sol} + e^{-}$$

Will stop here today, I want you to take up a very simple simplest reaction possible with two and intermediates so I need three steps. This I want to see another mechanism, which is called catalytic mechanism which is little different little tricky. Once you know how to handle 1 adsorb two adsorb catalytic mechanism and the E-EA R which we saw just know you should be able to write impedance expression and current for any mechanism with any number of species.