Electrochemical Impedance Spectroscopy
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Lecture – 28
Catalytic Mechanism

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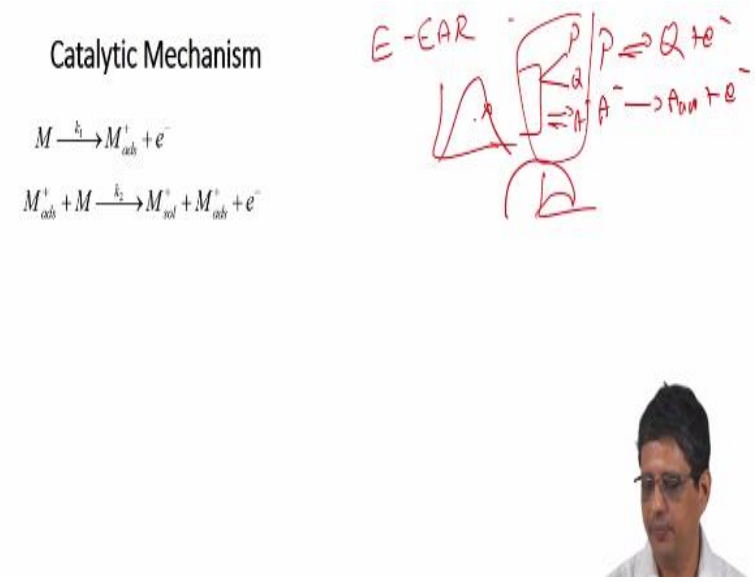

Catalytic Mechanism

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

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

I want to show you the mechanism, which is called catalytic mechanism in the literature. This is little different from what we have seen so far. What we have seen so far, is very simple equation, where directly something goes into solution, or it can be A becoming B + electron where these are charged species with A and B differ by one charge. It is similar to this. We have seen a case where it goes through one intermediate, $M^{+}_{sol}, M^{2+}_{sol}$. If you have M^{2+}_{sol}, it is going to be with electron. This is another mechanism. Third mechanism is what we just saw where you have 2 intermediate species. With one intermediate species, you get 1 equation, you can rearrange it and with two intermediate species, you get 2 equations and 2 unknowns.

You realize that it has to be solved using matrix formulation or something equivalent to that. It involves n number of linear equations in dθ/dE, you can solve them and get the answer. Once you know how to do it for 2, you can do it for any number. It just becomes lengthier, but it is not more difficult in terms of understanding and approaching the problem. This is little different.

In addition to this, we also saw one mechanism, which we denoted as this, where you have a reaction reversible, irreversible. We have taken irreversible reaction in that example, because it was little easier. Even this reversible, you can handle it. We have one reaction happening here; P going to Q. We also have A- adsorbing on top and this becomes reaction in parallel.

We have seen that, and in that case, we saw that current can increase and decrease, and therefore it can give rise to impedance like this, if you are taking in this DC potential. I want to show you a mechanism called catalytic mechanism, where you can get similar negative resistance values. First, I want to take a mechanism, which is not really going to give you a good steady state current. This is easy to explain with respect to what happens in the physical system and then we will use a slight variant of this.

The first reaction is metal goes into M_{ads}^{+} plus electron. We have seen this before. Metal loses an electron, it is an ion on the surface, it has not really come out from solution. It just loses an electron and we call it as M_{ads}^{+}. The M_{ads}^{+} in conjunction with the vacant metal, gives you an electron and it becomes M_{ads}^{+}, M_{sol}^{+} and electron, I want to explain this in detail with picture.

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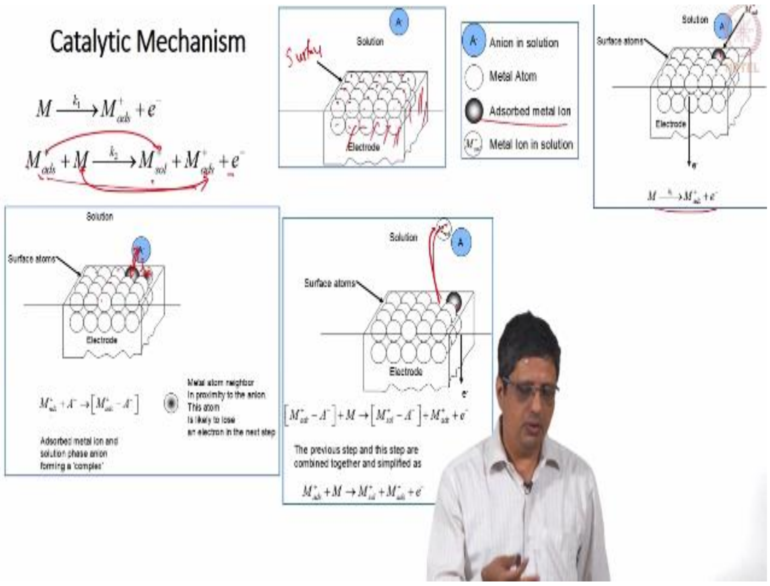

Catalytic Mechanism

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

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

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

$$M_{ads}^{+} + A^{-} \rightarrow [M_{ads}^{+} - A^{-}]$$

Adsorbed metal ion and solution phase anion forming a 'complex'

Metal atom neighbor in proximity to the anion. This atom is likely to lose an electron in the next step

$$[M_{ads}^{+} - A^{-}] + M \rightarrow [M_{sol}^{+} - A^{-}] + M_{ads}^{+} + e^{-}$$

The previous step and this step are combined together and simplified as

$$M_{ads}^{+} + M \rightarrow M_{sol}^{+} + M_{ads}^{+} + e^{-}$$

In the top level, these atoms are surface atoms. This is inside. This is exposed to solution on here, and this is covered with insulator on the side, [Just that we are seeing it from the side visualization, it is okay] and there is an anion like chloride ion. First step happens here and metal becomes M_{sol}^{+} + electron. One electron is lost from this location. Therefore, this has become ion and I am denoting it by grey colour.

As it is positively charged, it is likely that the anion comes closer to this. Next, notice that top right corner is a metal now. One to the left of that is M_{ads}. When the anion comes here, the anion is negatively charged. It comes close to this and it is somewhat close to the top right atom because this is negatively charged. It is easy for the electron to be taken out and it will repel the electron. It is easier for this atom to lose an electron compared to other neutral atoms. That is at least the hypothesis. This is not completely ionized state. I am just marking it in a slightly different colour to tell you that it is likely to lose an electron. I am splitting this step into 2 steps for our visualisation. Therefore M_{ads} + A- forms a bond. The neighbour metal atom, which is in proximity to the anion, is likely to lose an electron. What happens is, this loses an electron and this becomes M_{ads}. Therefore, M_{ads} + M in presence of anion, anion does not really come and sit on the surface and block for long enough time. We say there is one atom here and one ion here. Anion comes because it comes, close to this, it repels this electron and the atom loses an electron. This cation, which is already M_{ads} that bond with this, goes out into the solution, and exposes the metal below. What happens is, this was M_{ads} and this was metal. This has become M_{ads} and this has become metal. This has become metal means, this has gone out, and the vacancy at below is available and what was originally M_{ads}, has gone into solution.

It is as if one atom is here, another atom is here. This is ion, and this anion comes, and it pulls this out leveraging this, and this becomes M_{ads}. The original M_{ads} has not become metal. It has gone out into solution. If you look here, it is going to be written as M_{ads} + M to tell you clearly. This metal has become M_{ads} here. If the way I express the mechanism, if you use radioactive isotope and say, this atom is different, that atom is different, chemical properties are same, but I can identify which is what, then this metal has become M_{ads}. This M_{ads} has gone into solution, and this has given rise to a vacant metal site and electron is taken, because this has lost an electron.

It is called as catalytic because at the end of it, it is like metal going to metal solution, net M_{ads} has not changed. The fractional surface coverage of M_{ads} has not change. You got one M_{ads} here and one vacant site here. Now it looks like it just changed although it is not exactly the same, one has gone into the solution. The number of vacant sites and number of M_{ads}^{+} site have not changed at the end of this process. In chemistry, you would usually say catalyst. It will participate in a reaction, and it is not consumed at the end of it. [We know that catalyst is poisoned and we will ignore all those things]. Catalyst is something you put reactant, reaction happens. It will get involved in the reaction. Only then, it can make it faster and at the end of it, it is not like a reactant, which is consumed, this just comes back. Likewise, here, we are not increasing or decreasing the number of sites and therefore, it is called catalytic. You can also imagine that the anion is catalysing the reaction in terms of taking the metal into solution and pushing electron inside this electron. [Now you visualize this, I would like you to write the mass balance and charge balance equations for this].

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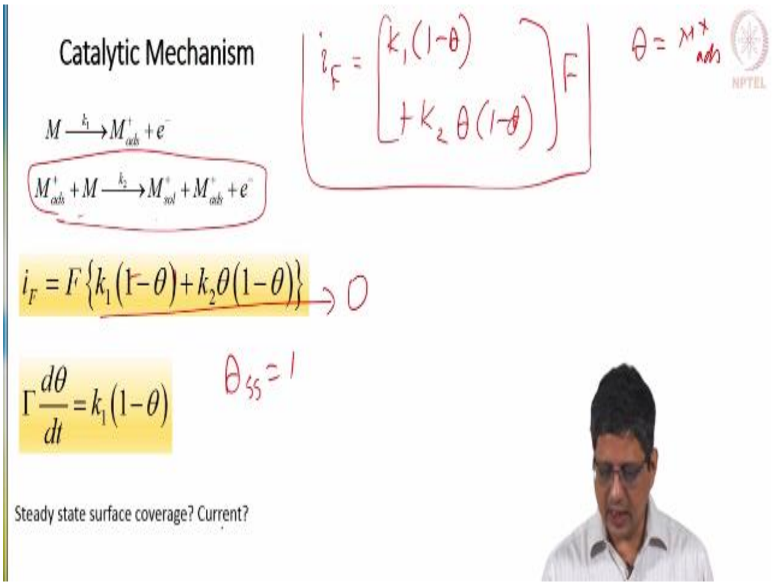

Catalytic Mechanism

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

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

$i_F = F\{k_1(1-\theta) + k_2\theta(1-\theta)\} \rightarrow 0$

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

Steady state surface coverage? Current?

$i_F = \begin{bmatrix} k_1(1-\theta) \\ + k_2\,\theta(1-\theta) \end{bmatrix} F$

$\theta = M_{ads}^{+}$

$\theta_{ss} = 1$

[What is going to be the charge balance equation?] I am going to call θ as the fractional surface coverage of M_{ads}^{+}. There is only one species here. I am taking a simple equation. You can have it for multiple species and you can say one of the step is catalytic step, which is fine. We want to take the simplest one. The vacant metal site is going to be called as 1- θ. Bare metal sit e is 1- θ. First step is going to give us an electron. Second step involves (refer video), it is a second order reaction. There are 2 species. If I say A going to B, it is a first order reaction as long as it is an elementary reaction. If you say A + B going to C, C or whatever, it is going to be second order because you have 2 species involved. The first one is going to be written as θ, second one is going to be written as 1- θ. All these things tell the number of electrons produced.

I multiply by Faradaic constant, I will get:

$i_F = [k_1(1-\theta) + k_2\theta(1-\theta)]\mathrm{F}$

What about the rate of change of θ? Second step does not produce or consume θ, or does not produce or consume M_{ads}^{+}. Net effect is, it does not do that. [First step will produce, am I correct, am I missing something? This is not the place to write].

What will be the steady state concentration of θ? What happens is first step produces M_{ads} and if site is vacant, it is going to become M_{ads}, if not now, a little later. There is a particular rate at which it happens. The second step, whenever it sees a vacant site, then only the second step happens. You need a vacant site in conjunction or right next to an adsorbed site, both are necessary. Whenever there is a vacant site, the second step will proceed. If there is no vacant site or if there is no adsorbed species, second reaction will not proceed. It needs both of them right next to each other. Therefore, I cannot have it completely bare metal and then the second step will not happen. If I have it completely covered with M_{ads}, second step will not happen. In the beginning, production of M_{ads} will always keep happening by the first reaction.

It may happen at a slower rate or a fast rate depending on the value k and anything that is vacant will be converted to adsorbed species. Anything that is adsorbed, net it will not be converted. It will not be consumed, which means eventually the entire surface will get covered with adsorbed species and you will not have any further reaction. If everything is adsorbed, θ = 1, 1- θ is going to be 0. There is no bare metal site.

Imagine you have 100 sites and 99 of them are already adsorbed. One site is there, because of that the second step can still happen. However, sometime or other, the bare metal is going to become via the first step, it is going to become M_{ads} and then it will stop. The steady state solution is $\theta_{ss} = 1$. It means, current is going to be 0. I use this mechanism to illustrate how the second step should be visualized and how to write the mass balance equation and charge balance equation for the second step. We have done many examples for the first step by now. The steady state surface coverage and current values are not that good.

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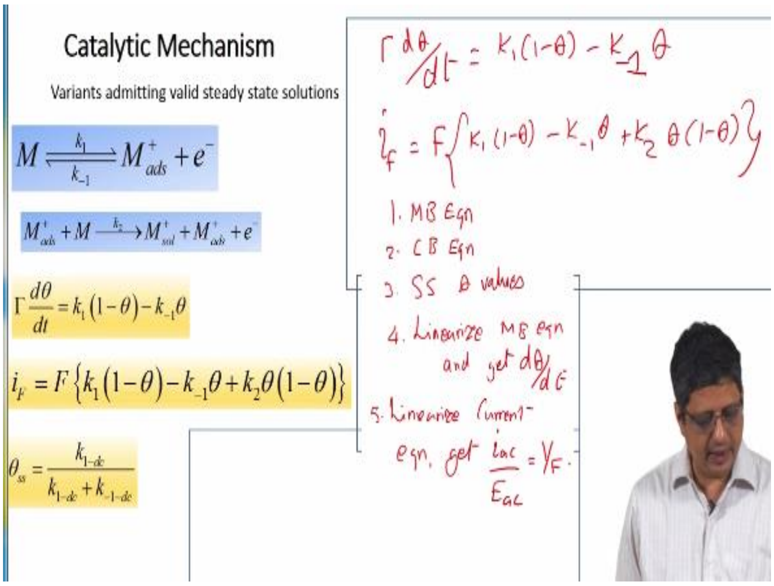

Catalytic Mechanism

Variants admitting valid steady state solutions

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

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

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

$i_F = F\{k_1(1-\theta) - k_{-1}\theta + k_2\theta(1-\theta)\}$

$\theta_{ss} = \frac{k_{1-dc}}{k_{1-dc}+k_{-1-dc}}$

$\Gamma d\theta/dt = k_1(1-\theta) - k_{-1}\theta$

$i_F = F\{k_1(1-\theta) - k_{-1}\theta + k_2\theta(1-\theta)\}$

1. MB Eqn
2. CB Eqn
3. SS θ values
4. Linearize MB eqn and get $d\theta/dE$
5. Linearize current eqn. get $\frac{i_{ac}}{E_{ac}} = Y_F$.

[I should have put in animation for this]. I want to propose another variant, where you will get a non-zero steady state current. Let us see if first reaction is reversible. It means, if you have M_{ads} species, it can become bare metal by taking up an electron. [For this I would like you to write mass balance equation and the charge balance equation]. We know the process by now, so you got the mass balance equation and charge balance equation and you can do the steady-state θ value, simple rearrangement, I would like you to get dθ/dE, this is also similar to what you have done for one adsorbed species. So please go ahead and write the equation for dθ/dE, by taking this mass balance equation and expanding it in Taylor series, and truncating it.

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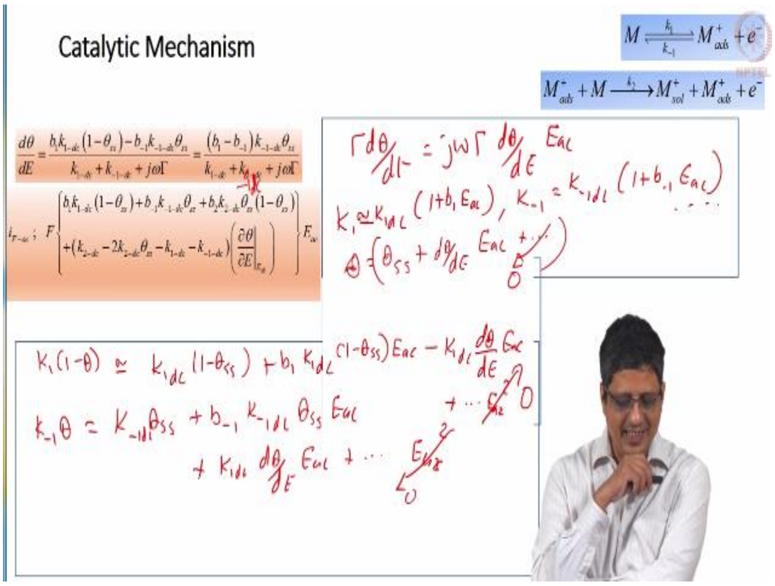

Catalytic Mechanism

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

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

$\frac{d\theta}{dE} = \frac{b_1 k_{1-dc}(1-\theta_{ss}) - b_{-1}k_{-1-dc}\theta_{ss}}{k_{1-dc}+k_{-1-dc}+j\omega\Gamma} = \frac{(b_1-b_{-1})k_{-1-dc}\theta_{ss}}{k_{1-dc}+k_{-1-dc}+j\omega\Gamma}$

$i_{F-ac} ; F\left\{\begin{matrix} b_1 k_{1-dc}(1-\theta_{ss}) + b_{-1}k_{-1-dc}\theta_{ss} + b_2 k_{2-dc}\theta_{ss}(1-\theta_{ss}) \\ +(k_{2-dc} - 2k_{2-dc}\theta_{ss} - k_{1-dc} - k_{-1-dc})\left(\frac{\partial\theta}{\partial E}\Big|_{E_{dc}}\right)\end{matrix}\right\}E_{ac}$

$\Gamma d\theta/dt = j\omega\Gamma \, d\theta/dE \, E_{ac}$

$k_1 \simeq k_{1dc}(1+b_1 E_{ac}),\ k_{-1} = k_{-1dc}(1+b_{-1}E_{ac}) \ldots$

$\theta = (\theta_{ss} + d\theta/dE \, E_{ac} + \ldots \cancel{E^2} \to 0)$

$k_1(1-\theta) \simeq k_{1dc}(1-\theta_{ss}) + b_1 k_{1dc}(1-\theta_{ss})E_{ac} - k_{1dc}\frac{d\theta}{dE}E_{ac} + \ldots \cancel{E_{ac}^2} \to 0$

$k_{-1}\theta = k_{-1dc}\theta_{ss} + b_{-1}k_{-1dc}\theta_{ss}E_{ac} + k_{1dc}\, d\theta/dE \, E_{ac} + \ldots \cancel{E_{ac}^2} \to 0$

Therefore k$_1$, k$_{-1}$, k$_2$, are dependent on potential as they are involved in electrochemical steps and you would write like this. There is only one θ, so you do not have to write it as θ$_1$. You can write the expression for $k_1(1-\theta)$, $k_{-1}\theta$ and on the right hand side, substitute for both terms and then rearrange. [It is going to t ake you few minutes, but you can do that and you should get an expression that is given here as long as I have done that correctly]. See if you get the expression correctly and give the kinetic parameters. If you write in a programming environment like Matlab, or C^{++}, within a second, as long as you get the kinetic parameter, set of frequencies, you would get the result. [It is just you want to do it correctly, when you write the equations you may have to spend some time to do this correctly. You may have to spend some time to program, but it does not take time to calculate it. Do you get dθ/dE? If you get it, let me know].

"Professor - student conversation starts"

In the final expression, k_{2dc} would not be there, it is k_{-1dc}. Thanks.

"Professor - student conversation ends"

In the mass balance equation, k_2 does not come, because $k_{1dc}(1-\theta_{ss})$ is equal to $k_{-1dc}\theta_{ss}$, we can write in a slightly simplified form. [It is more useful when you write in paper, when you put in a program, it does not matter. It is all the same. I assume that if you are given enough time whoever has not completed yet will complete it. This is a little more fun. Let us see if I have space in the next one].

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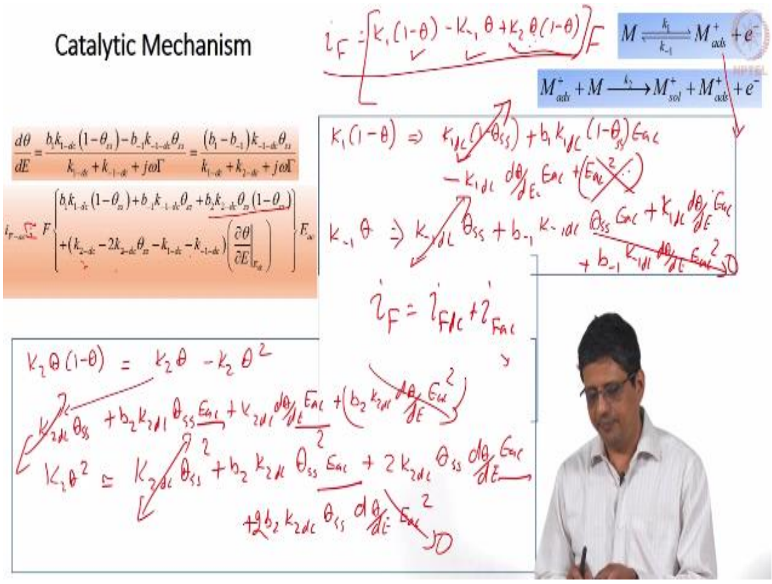

Catalytic Mechanism

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

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

$$\frac{d\theta}{dE} = \frac{b_1 k_{1\text{-}dc}(1-\theta_{ss}) - b_{-1}k_{-1\text{-}dc}\theta_{ss}}{k_{1\text{-}dc}+k_{-1\text{-}dc}+j\omega\Gamma} = \frac{(b_1-b_{-1})k_{-1\text{-}dc}\theta_{ss}}{k_{1\text{-}dc}+k_{2\text{-}dc}+j\omega\Gamma}$$

$$i_{F\text{-}ac} \cong F\left\{\begin{matrix} b_1k_{1\text{-}dc}(1-\theta_{ss}) + b_{-1}k_{-1\text{-}dc}\theta_{ss} + b_2k_{2\text{-}dc}\theta_{ss}(1-\theta_{ss}) \\ +(k_{2\text{-}dc} - 2k_{2\text{-}dc}\theta_{ss} - k_{1\text{-}dc} - k_{-1\text{-}dc})\left(\frac{\partial\theta}{\partial E}\Big|_{E_{ss}}\right)\end{matrix}\right\}E_{ac}$$

$i_F = [k_1(1-\theta) - k_{-1}\theta + k_2\theta(1-\theta)]F$

$k_1(1-\theta) \Rightarrow k_{1dc}(1-\theta_{ss}) + b_1 k_{1dc}(1-\theta_{ss})E_{ac} - k_{1dc}\frac{d\theta}{dE}E_{ac} + \cancel{(E_{ac}^2)}$

$k_{-1}\theta \Rightarrow k_{-1dc}\theta_{ss} + b_{-1}k_{-1dc}\theta_{ss}E_{ac} + k_{1dc}\frac{d\theta}{dE}E_{ac} + b_{-1}k_{-1dc}\frac{d\theta}{dE}E_{ac}^2 \to 0$

$i_F = i_{Fdc} + i_{Fac}$

$k_2\theta(1-\theta) = k_2\theta - k_2\theta^2$

$k_{2dc}\theta_{ss} + b_2k_{2dc}\theta_{ss}E_{ac} + k_{2dc}\frac{d\theta}{dE}E_{ac} + (b_2k_{2dc}\frac{d\theta}{dE}E_{ac}^2)$

$k_2\theta^2 \cong k_{2dc}\theta_{ss}^2 + b_2k_{2dc}\theta_{ss}^2E_{ac} + 2k_{2dc}\theta_{ss}\frac{d\theta}{dE}E_{ac}$

$+2b_2k_{2dc}\theta_{ss}\frac{d\theta}{dE}E_{ac}^2 \to 0$

Whole thing within the bracket multiplied by Faradaic constant tells you the current. I would like you to expand here, leave dθ/dE as it is, because we know we can substitute from the previous page. The only thing you need to take care is, $\theta(1-\theta)$. You can either multiply that, and write it as $\theta - \theta^2$ and then do this, or you can just take it as θ_{ss} + $d\theta/dE_{ac}$ as long as you make sure that the E_{ac}^2 and higher order terms are thrown away. You have $k_2\theta(1- \theta)$ and each one of them will give you an E_{ac} term. You will get up to cubic term. It does not matter. You retain constants, you retain the E_{ac} term. Anything, which is higher order, you throw it away, neglect it, and then you will see that the terms that you get here. It can be segregated as DC and AC, and you will get the expression for this. It is approximately equal to (refer video); you get 4 terms out of which you retain 3. You can split the last one into 2. You know how to handle first one. It is like writing k_1, k_{-1} whatever into θ, second one we are going to get $k_2\theta^2$. I will write the steady state part first. You know what you get when you take a derivative of y with respect to x. You will write it as dy/dx. If it is $y^{2,}$ you are going to write it as 2ydy/dx. If it is θ^2, when you take the derivative, I would write it as 2θdθ/dE. That is one way of looking at it. Another way is to just expand θ as θ_{ss}+ dθ/dE × E_{ac} then θ^2, multiply them, and then retain the constant, and the E_{ac} term, and then throw away the E_{ac}^2 term. You are going to end up with something like this. It is a second order reaction. Therefore, you are going to get only dθ/dE. To determine the dθ/dE, you do not have to worry about this at all. To determine the current, you will have to look at this as the second order equation, and you will get an expression which is little lengthy. You have to do it with care, but you will get the expression here. Look at the i_F first and after you rearrange this, you can write i_F as i_{Fdc} + i_{Fac} where i_{Fac} depends on E_{ac}, i_{Fdc} is independent of E_{ac}. You can rearrange and get. After sometime, you will be able to get. The first part out here; this part $k_{1dc}(1- \theta_{ss})$ goes away into i_{dc}. This part goes into i_{dc}, this goes into i_{dc}, this goes into i_{dc}. Whichever depends on E_{ac} 1, 2, 3, 4 terms here, 1, 2, 3, 4 terms here, you would get dθ/dE from the first term, you will get dθ/dE from the second term. You would get 2 terms for dθ/dE from this expression of $k_2\theta(1-\theta)$. We will get 4 terms here in dθ/dE, and other things you can rearrange, you can simplify a little bit, using the steady state condition. Sometimes you can get a little simpler expression. [I am just grouping them together here; it is little different. Are you able to get it? If it needs time let me know, but I would like you to do that and see, because if you face problem, better to sort it out here].

As long as you assume, solution resistance is negligible, and the mass transfer is rapid, and if you know how to handle the catalytic reaction mechanism given here, and if you know how to handle 2 adsorbed intermediates, you should be able to propose any mechanism, and write the impedance expression for that mechanism, regardless of how complex it looks. Catalytic is slightly tricky one. What you have seen before is 2 adsorbed intermediate. You can handle single adsorbed, multiple adsorbed. You had seen E-EAR, which is one reaction, electrochemical reaction or electron transfer reaction occurring in parallel with adsorption reaction.

Now you can propose some reaction saying there are 5 steps, 4 intermediates, or 3 intermediates, maybe one reaction is happening, catalytic reaction is happening along with the regular reaction. In this example, we have said metal become M_{ads} and it is reversible. I can also say, along with this catalytic mechanism, I have a regular reaction where M_{ads} becomes M_{sol}, and that is another reaction mechanism. Like that, I can come up with many variants; you can come up with your own variants. You would be able to write the expression for all of them. You would be able to tell the impedance, provided kinetic parameters are given. [In order to ensure that, you can do that, I would like you to derive and make sure that you get the expressions correctly].

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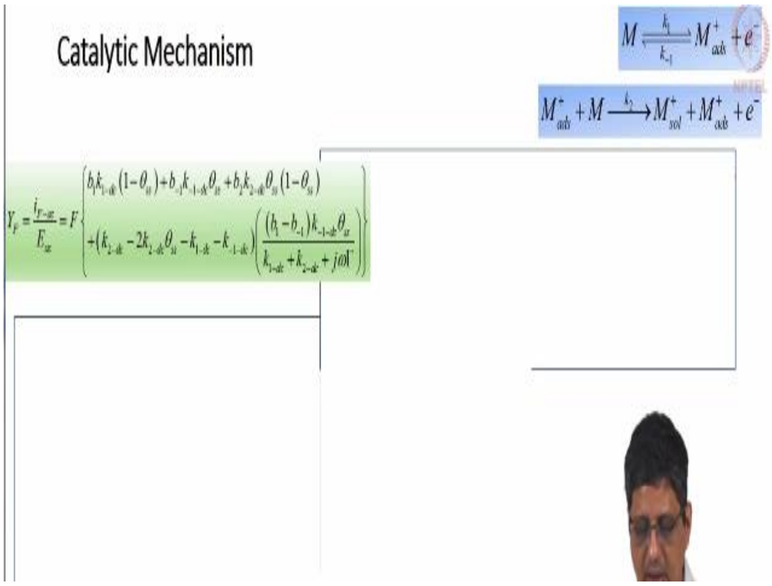

Catalytic Mechanism

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

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

$$Y_F = \frac{i_{F-ac}}{E_{ac}} = F\left\{\begin{array}{l} b_1 k_{1-dc}(1-\theta_{ss}) + b_{-1}k_{-1-dc}\theta_{ss} + b_2 k_{2-dc}\theta_{ss}(1-\theta_{ss}) \\ +\left(k_{2-dc} - 2k_{2-dc}\theta_{ss} - k_{1-dc} - k_{-1-dc}\right)\left(\dfrac{(b_1 - b_{-1})k_{-1-dc}\theta_{ss}}{k_{1-dc} + k_{2-dc} + j\omega\Gamma}\right)\end{array}\right\}$$

You can rearrange it; you can substitute for dθ/dE. That is what I have done here and given you the expression.

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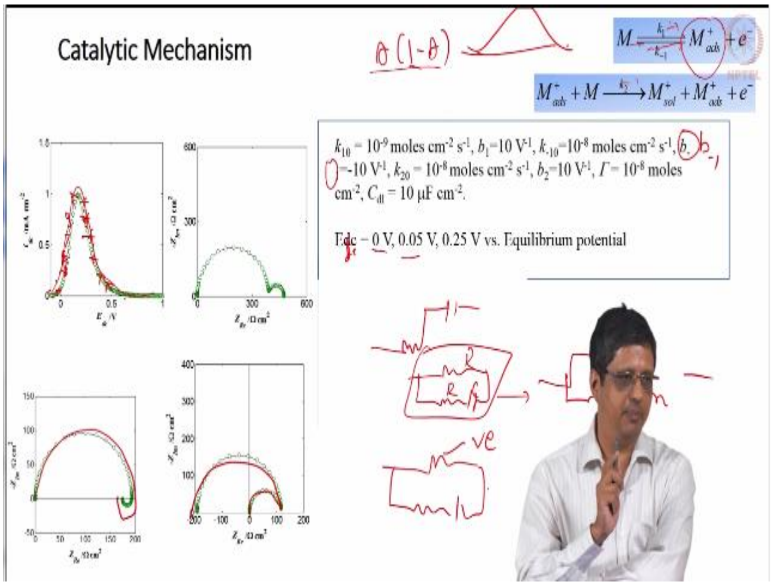

Catalytic Mechanism

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

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

$k_{10} = 10^{-9}$ moles cm^{-2} s^{-1}, $b_1 = 10$ V^{-1}, $k_{-10} = 10^{-8}$ moles cm^{-2} s^{-1}, $b_{-1} = -10$ V^{-1}, $k_{20} = 10^{-8}$ moles cm^{-2} s^{-1}, $b_2 = 10$ V^{-1}, $\Gamma = 10^{-8}$ moles cm^{-2}, $C_{dl} = 10$ μF cm^{-2}.

Edc = 0 V, 0.05 V, 0.25 V vs. Equilibrium potential

One set of kinetic parameters, k_1, b_1, k_{-1}, b_{-1}, [b_{-1}, it will be nice if it is given in 1 line but okay], k_2, b_2, Γ value and a reasonable double layer capacitance value give you a current like this. It means, when potential is very low, forward reaction is not happening to a large level. This reaction is not happening to a large level, we are not getting electrons. As k_1 is small, k_2 is small, current is more or less 0. When potential is very large, k_1 is large, k_2 is large, k_{-1} is small, [no problem at all]. When it is large, most of it is M_{ads}, and θ goes to more or less 1. It is not going to remain at 1 because some of it, when it is close to 1, some reaction will happen in the reverse direction. It is not 0, it is a small value, but θ is almost 1. Therefore net current is almost 0. Under steady state condition, if I go to 1 E_{dc}, this is the value I get, and I go to another higher potential, higher potential, higher potential, current keeps on increasing. After sometime, when surface coverage becomes significant, this current value keeps decreasing. This is similar to what you have seen for E-EAR, although it is a different mechanism. It involves different type of species.

This can also give rise to curve like this. Here, if I go to E_{dc}, at 0 potential, I get 2 semicircles here; 0.05 slightly away from this, so this is here, somewhere here, I get a capacitance with an inductive loop; 0.25 is probably somewhere here. I get a capacitance with a negative resistance. If you use electrical circuit for this, you are going to use a resistor, and resistor capacitor (refer the circuit in video), forget the solution resistance and double layer capacitance. This spectrum you are going to say, this is what I am going to use. This spectrum you are going to say I will use this, but I will come up with a negative value here, and you have to reconcile, the same system at different potential, why does it behave like a capacitor, why does it behave like a negative resistor, why does it behave like an inductor?.

That approach is not a good approach. It is not behaving like an inductor or it is not behaving like a negative resistor. It is giving you a spectrum that can be generated by a circuit with inductor. It can be generated by a circuit with capacitor, or it can be generated by a circuit with negative resistance. It does not mean that this reaction or this system has an inductor inside or has a negative resistance inside. It is a simple kinetic reaction; kinetic parameters and the potential are such that they give rise to spectrum like this. Physically you can tell what is happening here, what is happening here, what is happening here. Here you can say when I increase the potential, adsorbed species become more. The current increases little bit because of that, but the second step which gives current, that is decreasing a lot, so whenever potential is increasing the reaction, forward reaction rate constant k_1 and k_2 are increasing, and physically it is meaningful.

The combination works in such a way that, one current increases a little, another current decreases a lot because the θ values also is playing a role, and θ value increases that causes the second reaction to go down. $\theta(1- \theta)$ will show a maximum. When θ is half, it is this particular thing is going to show a maximum. When θ is 1, it is 0, when θ is 0, it is 0. The net current decreases at low frequencies because of that. Using one set of kinetic parameter, I can generate spectra at many potentials. If I am using the circuit, each one I have to come up with one R-value, another R-value, another C value, and then slightly higher one, I will have to come up with another value. At some point, this capacitance is going to become like an inductor or it has to become a negative resistance and capacitor. I will have to come up with some explanation. If I am restricting my mind to looking only at electrical elements, I will have difficulty in explaining what is happening. If I tell this is probably coming from a kinetic and I can explain this reaction using kinetic parameter, I can use one set of kinetic parameters for all these potentials, all the spectrum. All the spectra that I get here can be generated from one set of kinetic parameters.

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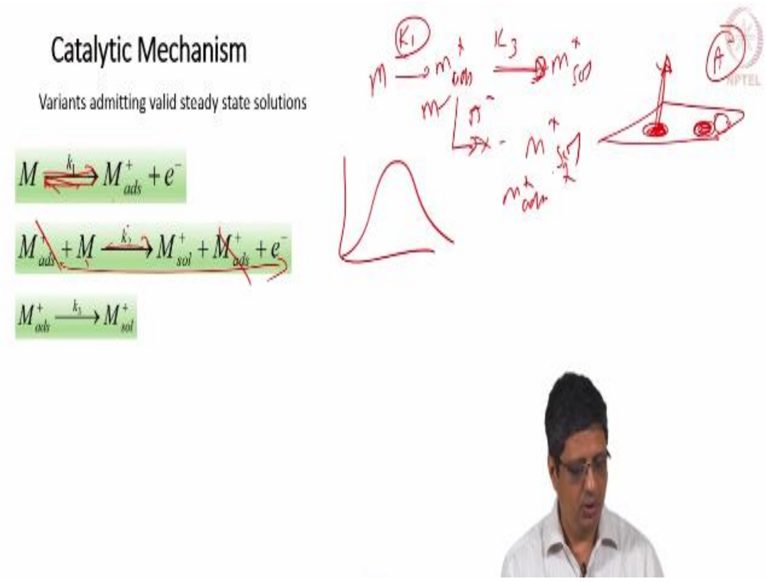

Catalytic Mechanism

Variants admitting valid steady state solutions

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

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

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

Another variant, it is just one example I have shown, where, if you have forward reaction and the second step that does not give you a valid steady state solution with the non-zero current. If I make it reversible, I have to produce a metal site, this does not consume adsorbed species, in the forward reaction only produces adsorbed species, I can consume it by making it reversible. I can say M become M_{ads}, and it can go into solution as a normal step. This is the first mechanism we have seen for one adsorbed intermediate. In addition, this goes via the catalytic path. It means, if I have a surface, if this is M_{ads}, it will go, this is also M_{ads}, this is bare metal. Bare metal can become M_{ads} by the first step here. M_{ads} can directly go into solution even in the absence of anion by this step. If I have anion, the anion can come and if the neighbour happens to be a vacant site, it can also go via this step. This is parallel step. M_{ads} is going in to M^+_{sol}, but it re-generates an M_{ads} here by working with the bare metal site here. The net effect is to do the algebra and cancel out this. It is like M going to M^+_{sol} with an electron. This also will give you a steady state solution, which means a steady state solution where θ is not 1, where current is not 0, for reasonable values. If you go to extreme value, current will go towards 0, (()) it would not be settling at 0. This again, depending on the kinetic parameter value, you will get current like this; you will get negative resistance. It is possible to explain negative resistance by different types of mechanism. You will have to have some idea about the system, and you will have to say that there is one reaction happening; species P becoming species Q. In addition, I have P becoming Q is the E-EAR reaction where we say P and Q are in solution. In addition, if you put this chemical A-, then I am seeing this pattern, that is one. Second, we are not adding any chemicals here specifically to adsorb. It is just that A- happens to be in solution and you see this behaviour because of catalytic reaction. If you do not have A-, you do not have this. You will have to come up with some idea, you have to come up with some proposal for a mechanism and then see if that mechanism can explain the results here.