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

Lecture – 29
Examples with Frumkin or Temkin Isotherms

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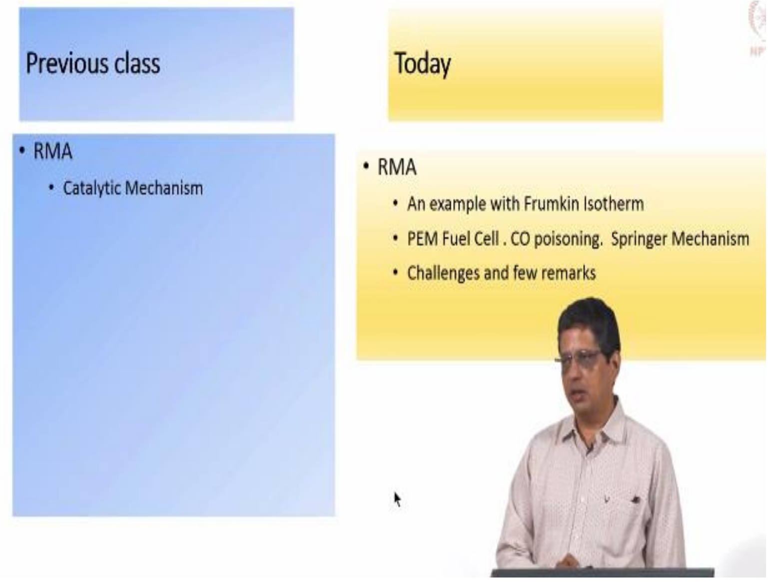

Previous class

- RMA
  - Catalytic Mechanism

Today

- RMA
  - An example with Frumkin Isotherm
  - PEM Fuel Cell . CO poisoning. Springer Mechanism
  - Challenges and few remarks

We have seen in earlier classes, a mechanism called catalytic mechanism, so we have (also) seen few examples before. One, which is the simple electron transfer reaction. The next is the two-step reaction with one adsorbed intermediate. We also seen three-step reaction with two adsorbed intermediates. We have seen two other type of reactions; one is adsorption along with electron transfer, which you call as EAR. Another is what you call as catalytic mechanism, where you have anion coming in and it needs adsorbed species and a vacant species sitting next to each other for the reaction to proceed. In these examples we saw that it can give rise to current versus potential curve, where current increases and then decreases with respect to potential and this causes a negative impedance.

Now I want to take up an example where we do not assume it is Langmuir isotherm. Langmuir isotherm model is easy to work with, but when we look at the situation actually, this adsorbed species are charged species and they will interact. They will typically repeal each other. If (at) one location you have M adsorbed, it is likely that another adsorbed species or another atom will lose an electron if it is far away from this. If it is right next to this, it may not lose an electron that easily. We are able to manage with Langmuir isotherm model to simulate lot of the observed results, but we should also know how to handle the cases where the rate constant depends on the surface coverage. In some situations, it is necessary to use that. One example is in PEM fuel cells. You have a reaction where hydrogen is oxidized, oxygen is reduced. In a case where you have a hydrogen stream coming in, it may have trace amount of carbon monoxide, and CO poisoning can affect this reaction. In those cases, the rate constants or some of the rate constants depend on the surface coverage of the species and that is necessary to incorporate to describe what we see. Before we go to that example, I want to start with the simpler example. (With that, we will complete the set of examples we see for RMA and then describe few challenges that one faces when you actually try to optimise the kinetic parameters and fit the model to this data).

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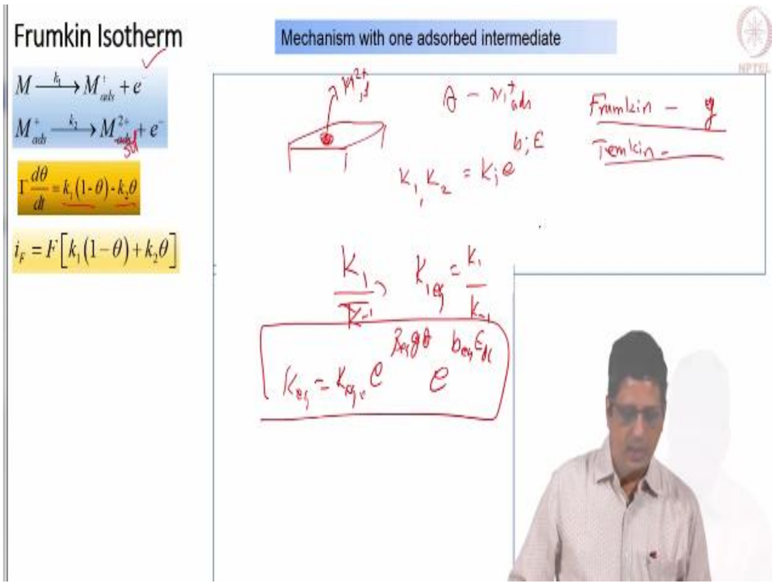

Frumkin Isotherm

Mechanism with one adsorbed intermediate

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

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

$$\Gamma \frac{d\theta}{dt} = k_1(1-\theta) - k_2\theta$$

$$i_F = F\left[k_1(1-\theta) + k_2\theta\right]$$

First, I want to start with this example, we have seen this before (refer video, 03:02). It is the first case where we looked at adsorbed intermediate. You have metal losing an electron and become metal^{+} adsorbed, it loses one more electron and goes into the solution as M^{2+} solution, and therefore it will become a vacant site again.

Now, for the first reaction we know the rate of the first reaction is given by $k_1(1- \theta)$, and the rate of the second reaction is given by $k_2\theta$ where ‘θ; is the fractional surface coverage of M^{+} adsorbed species. This is the only adsorbed species that we are looking at, the remaining is the vacant metal and we know $\Gamma(d\theta/dt)$ = this (refer video, 04:02). We can write the current. Current from the first step is $k_1(1-\theta)$, from the second step the rate is $k_2\theta$. Both of them give (involve) electron, therefore, we have to add them (and) multiply by Faraday constant to get the total current out of the overall reaction. This is the Faraday current from this. Now, we had assumed earlier that the k_1, k_2 etc are dependent on potential and otherwise they are not dependent on surface coverage or anything, that is the reason we can apply Langmuir isotherm model.

Now Frumkin isotherm, the interaction between the adsorbed species cannot be neglected. Adsorbed species may repel next species or it may attract, typically, it will repel, it has a parameter called ‘g’. If ‘g’ is positive, it means that the adsorbed species will repel each other. If it is negative, it means it will attract each other and that will facilitate the formation of that species. If it is 0 it becomes Langmuir isotherm.

There are actually many other isotherm models. Another model is Temkin isotherm. Temkin isotherm assumes that there is no interaction between the species, but the sites that are available on the surface which are not uniform; they are not identical. Some sites are more favourable for adsorption; some sites are less favourable for adsorption. Therefore, when new adsorbed species forms, it is going to first form in the location where it is more favourable. When that is completely filled up adsorbed species will go to the next level where it is little harder. However, with more effort it can form again. That means the rate constant will change once the surface coverage is significant. Meaning in has filled up all the easy areas, therefore it will become harder so it will become slower. ‘θ’ here will affect the rate constant value.

Actually all that they describe is how the equilibrium constant in a reversible reaction if you take k_1/k_{-1}, Temkin isotherm or Frumkin isotherm basically describe the equilibrium constant, they do not describe the rate constant. Rate constant is for kinetics. Equilibrium constant is a thermodynamic value; however, if you take the rate constant to be a function of θ, and with the parameter β_1, (I will describe what that is shortly). If you give a rate constant like this, then the equilibrium constant also will come in this form (refer video, 07:20). Right now I was taking the reverse reaction is negligible because we are operating in the region where it is very positive potential and forward reaction is significant. If you take k_{-1} to be 0, k_{-1} to be like this, and if you take the ratio of k_1 and k_{-1} to get the equilibrium constant. Then you would find that the form of the equilibrium constant is also going to be like this. At a given $_{dc}$ potential, (this is of course not here) it is going to exponentially depend on θ, and exponentially depend on potential. Depending on the value of β_1, β_{-1} etc. Since we know it is going to depend on ‘θ’, β_{eq} cannot be zero. It is going to depend on E_{dc}, b_1 and b_{-1} in fact they will have opposite signs, b_1 is going to be positive, b_{-1} is going to be negative. $(b_1 - b_{-1})$ will not be zero. All that the isotherms described is that is it going to be exponentially dependent on θ, exponentially dependant on potential because it is for electrochemical reaction. The form of Frumkin equation and Temkin equation will be same. Meaning, you can have a rate constant dependent on the surface coverage because the species interact. You can have the rate constant dependent on surface coverage because the sites are not equal, but both of them will give rise to the same expression at the end. You cannot really distinguish based on simple evaluation of a rate constant or equilibrium constant as a function of θ, you cannot say this is Frumkin isotherm, or this is Temkin isotherm, this will look similar.

If you have other way of finding and identifying that the sites are different, then you can say it is Temkin. If you have some way of proving sites are equal, but the moment I put one species I am not able to put another species next to that by some other technique then you can say yes, Frumkin isotherm is operational here. As an analogy, sometimes I give this example. If you go to a canteen where, let us say all the seats are equal. If some are occupied if you know them, there are friends you have likely to go next to them, if you do not know them or you know them and you do not like them, you are likely to go to the place away from them. This is one type of description. When someone sees from outside they do not know the individuals, they just see that, if it is occupied, the person is going to be far away. If it is empty, there are going to sit randomly in some place. This will represent Frumkin isotherm.

Another example, you go to a place and you know all of them [they are equally friends]; however, let us just say there are only few of them there and the seats are not equal meaning some seats have better view, some seats have poorer view, you are likely to go to that seat which has a better view first. Anybody who comes in will choose that. When that is full, we will go to the next one. When pretty much everything is full, they will go to the one, which has a very poor view. That is going to be an example for Temkin isotherm. When somebody looks from outside all that they will see is here of course if you know which site is what then somebody who looks from outside will know that people always preferentially go to that site.

But if they only have data on it is occupied, this is how it looks like (refer video, 11:04), if it is not occupied this is how it looks like, then they will not be able to see a difference between the rate constant or the preferential occupation in Temkin isotherm case and in Frumkin isotherm case. Because in our visualisation or in the example I mentioned we already think we know which site is better or which site is poorer or we can identify the sites. However, if you are not able to identify all that you have is it is going to be fast or it is going to be slow. Another way to say that is if it is empty, view is good; you are likely to go and sit there. If it is full, you will think should I really go in or should I wait and then go later, let it get empty and then I will go. That means the rate becomes slower. If it is fully empty whether it is Temkin or Frumkin, you will see same behaviour. You go quickly and occupy some place, you may occupy a special place or you may occupy random place, but you do not have to think and make a decision. If it is partially occupied, you will have to think and make a decision.

Coming back to this (refer video, 12:09), here we are going to assume that the species are going to repel each other. Meaning you have M^+ adsorbed formed in one location, you are not likely to have another. [I mean] it is possible that it will form, but it is not very easy. Its rate constant is going to be slower for that. We get the following description: k_1 and k_2 are dependent on potential as well as on 'θ', and 'g' is positive that describes that it is a repulsion. The reason this may happen is because of ΔG, free energy of formation of this species. It is linearly varying with θ. The first equation [first step] that is going to be the formation of θ. we expect when θ is more, k_1 will decrease.

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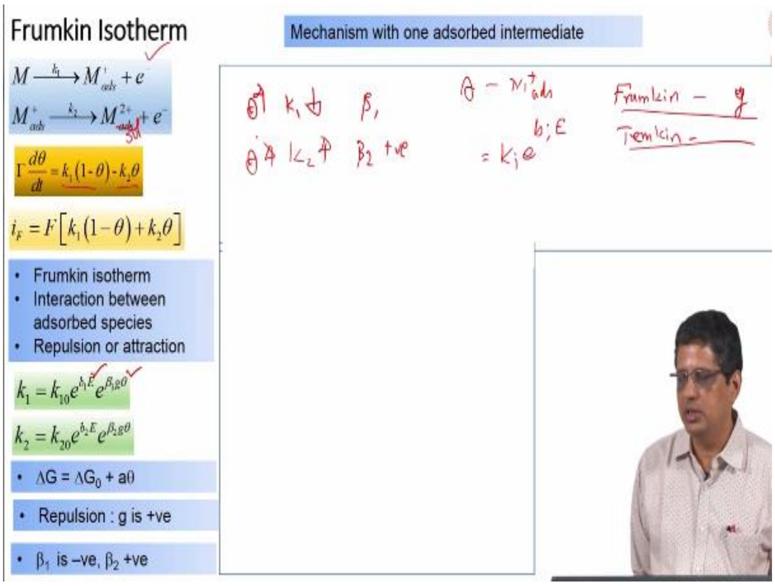

Frumkin Isotherm

Mechanism with one adsorbed intermediate

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

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

$\Gamma \frac{d\theta}{dt} = k_1(1-\theta) - k_2\theta$

$i_F = F\left[k_1(1-\theta) + k_2\theta\right]$

- Frumkin isotherm
- Interaction between adsorbed species
- Repulsion or attraction

$k_1 = k_{10} e^{b_1 E} e^{\beta_1 g\theta}$

$k_2 = k_{20} e^{b_2 E} e^{\beta_2 g\theta}$

- ΔG = $\Delta G_0 + a\theta$
- Repulsion : g is +ve
- β_1 is –ve, β_2 +ve

$\theta \uparrow \; k_1 \downarrow \quad \beta_1$

$\theta \uparrow \; k_2 \uparrow \quad \beta_2$ +ve

$\theta - M_1{}^+_{ads}$

$= k_i e^{b_i E}$

Frumkin – g

Temkin –

Therefore, we should say when θ increases, k_1 decreases, which means β_1 has to be negative, and g is positive. (If) I want k_1 to decrease when θ increases that is going to happen when β_1 is negative. k_2 on the other hand removes M^+ adsorbed. If you have lot of M^+ adsorbed in this, fractional surface coverage is high. Since they repel each other, it is easier for them to go out. [It is like this] Now you are going there, you do not like each other but you eat lunch anyway, you want to finish and go off quickly and if it more or less full you do not like each other you are thinking whether to go in or not when you are outside. The first step it is going to be slower, if it is full. Second step is going to be faster, if it is full.

Therefore, β_2 is going to be positive since k_2 increases when θ is high, [**Professor-student conversation**; no it is a Frumkin parameter]. If g is negative, it means it is attraction, when g is 0, it simply face to Langmuir isotherm. Frumkin isotherm does not tell us anything about k_1 and k_{-1} or k_2, it just tells K_1 equilibrium, K_2 equilibrium. We just propose that rate constant can be this form because this will lead to Frumkin isotherm. But, you might be able to come up with another expression for individual rate constants k_1, k_{-1}, k_2, and k_{-2} such that the equilibrium constant is still exponentially dependent on θ. We are just not using those things; this is a simpler way of doing it.

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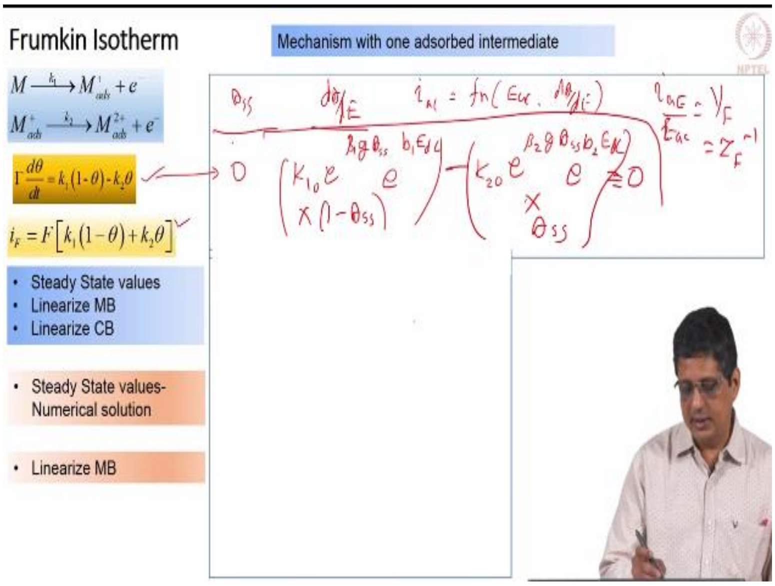

Frumkin Isotherm

Mechanism with one adsorbed intermediate

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$i_F = F\left[k_1(1-\theta) + k_2\theta\right]$

- Steady State values
- Linearize MB
- Linearize CB

- Steady State values-Numerical solution

- Linearize MB

θ_{ss} $\quad d\theta/dE$ $\quad i_{ac} = fn(E_{ac}, d\theta/dE)$ $\quad \frac{i_{ac}}{E_{ac}} = Y_F = Z_F^{-1}$

$0 = \left(k_{10} e^{\beta_1 g \theta_{ss}} e^{b_1 E_{dc}} \times (1-\theta_{ss})\right) - \left(k_{20} e^{\beta_2 g \theta_{ss}} e^{b_2 E_{dc}} \times \theta_{ss}\right) = 0$

So normally what we do here, we get these equations (refer video, 14:43), we first write steady state. We want to get θ_{SS}, then we will take this equation and take this equation, mass balance and charge balance, linearize them we will get an expression for $d\theta/dE$. We will get an expression for i_{ac} as a function of E_{ac} and it will have $d\theta/dE$. Then we will rearrange it so that we can get E_{ac}/i_{ac} or i_{ac}/E_{ac}. We will also get an expression for faradaic impedance or faradaic admittance. We have followed this procedure so far. First step is to get the steady state value, second step is to write these two equations and then linearize them, truncate, rearrange, get the values. To get the steady state values, I take this equation, set this to zero, since the potential is a constant [it is a DC]. 'θ' should be written as, of course I have not done this correctly, I will delete it, this term multiplied by (1-θ_{SS}), this term multiplied by θss, and if I subtract them that is going to go to zero. This equation we cannot solve it analytically. We will have to use numerical method to solve it. When you use numerical method, this is easy to solve though because θ_{SS} lies between 0 to 1.

You can take excel, this assumes of course, I have already given you k_{10}, g, β_1, b_1, k_{20}, β_2, b_2 [all those values are given to us], then for a given DC potential E_{dc}, you will have to find θ_{SS}. If you vary the value of θ_{SS} from 0 to 1, you will find it is crossing 0 at some location. You can find the value except that you cannot write an expression here and say that $\theta_{SS} = k_{1dc}/k_{1dc} + k_{2dc}$. Something similar you have done before, you cannot just write an analytical expression and say that this is the solution. However, it is possible to do it using any software or programming language, which you can use for plotting, or which you can use of programming, it is possible to do it quickly.

For example, if you take Matlab just take θ_{SS} going from 0 in steps of 0.001 till 1. You will see where it cross zero, and that is where it is going to be. It is a very simple way of doing it. You can also use an optimization program and get that. I do not think really that θ value of 6 or 10 decimal accuracy is necessary. You probably want to know it in 2 decimals, 3 decimals accuracy that is more than enough. Next is the step where we want to linearize mass balance equation.

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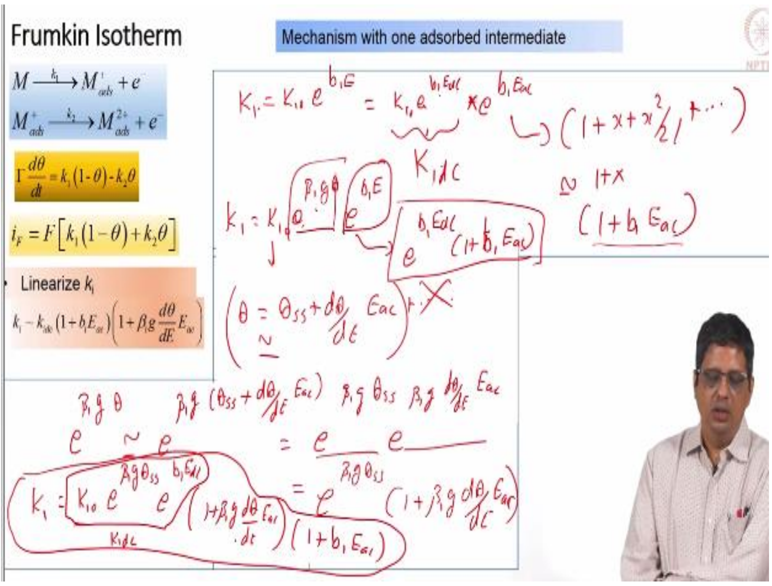

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$i_F = F\left[k_1(1-\theta) + k_2\theta\right]$

- Linearize k_1

$k_1 - k_{1dc}(1+b_1E_{ac})\left(1+\beta_1 g \frac{d\theta}{dE} E_{ac}\right)$

$k_1 = k_{10} e^{b_1 E} = \underbrace{k_{10} e^{b_1 E_{dc}}}_{K_{1dc}} \times e^{b_1 E_{ac}} \hookrightarrow \left(1 + x + x^2/2! + \dots\right)$

$\simeq 1+x$

$\underline{(1+b_1 E_{ac})}$

$k_1 = k_{10} \boxed{e^{\beta_1 g \theta}} \boxed{e^{b_1 E}} \rightarrow \boxed{e^{b_1 E_{dc}} (1+b_1 E_{ac})}$

$\left(\theta = \theta_{ss} + \frac{d\theta}{dE} E_{ac} + \cancel{\dots}\right)$

$e^{\beta_1 g \theta} \sim e^{\beta_1 g \left(\theta_{ss} + \frac{d\theta}{dE} E_{ac}\right)} = e^{\beta_1 g \theta_{ss}} e^{\beta_1 g \frac{d\theta}{dE} E_{ac}}$

$= e^{\beta_1 g \theta_{ss}} \left(1 + \beta_1 g \frac{d\theta}{dE} E_{ac}\right)$

$k_1 = \underbrace{k_{10} e^{\beta_1 g \theta_{ss}} e^{b_1 E_{dc}}}_{K_{1dc}} \left(1+\beta_1 g \frac{d\theta}{dE} E_{ac}\right)(1+b_1 E_{ac})$

Earlier, we would have taken k_1 and written as $k_1 = k_{10} \exp(b_1E_{dc}) \times \exp(b_1E_{ac})$. This part $\exp(b_1E_{ac})$, we would have taken as $1+ x + x^2/2! +\dots$ and then said that roughly this is 1+x.

That means I will write it as 1+ b_1 E_{ac}. This part we would have taken and said this I will call it as k_{1dc} because this is value of k_1 at the dc potential. This we know how to handle it. It is going to give us. This part is going to be approximately equal to this. This is a constant anyway. I would like to take this part and linearize it. When we linearize we are going to write like this. We are going to write θ as θ_{SS} + (dθ/dE) Eac + $(d^2\theta/dE^2)$ $E_{ac}^2/2!$ and then we are going to neglect higher order terms. Therefore, this is roughly equal to θ_{SS} + (dθ/dE) E_{ac}, E_{ac}, is a small number.

What happens to $\exp(\beta_1 g\theta)$? This is one approximately equal to this (refer video, 20:22). I have truncated the series. After substituting for θ in the truncated form, I can expand this and I can write this as the product of two terms. This I can leave it as it is, this I can again expand in Taylor series and truncate it. This I would write it as approximation here. Initially we write θ, expand it, and truncate it. Then we realise the θ actually comes in exponential form. We have to substitute anything that is small you can expand in Taylor series and truncate. Anything that is large you keep it as it is. θ_{SS} we do not know whether it is going to be large or small. E_{ac} we assume it is small. It is in our control we can make it as small as possible or as small as we want, as large as we want. Therefore, we are going to keep that as a small number here. k_1 I can write it as k_{10} $\exp(\beta_1 g\theta_{SS})$ $\exp(b_1E_{dc})$, and then I have 1+ β_1 g dθ/de E_{ac} that comes from the first part here, θ part here and then 1+ b_1 E_{ac} that comes from the second part [potential part]. Previously, I would have just had k_{10} remaining as it is, $\exp(b_1E)$ gives rise to one term here, (1+ b_1 E_{ac}). Here we have two E_{ac} terms, two terms each one having an E_{ac} term here, and earlier I would have said when we use Langmuir isotherm I would have said k_{10} $\exp(b_1E_{dc})$ is the value of k_1 at dc. Here the value of k_1 at dc is given by the term, which I had just covered here. This I would write it as k_{1dc}. If I apply a small ac previously it is going to vary around k_{1dc}, it is going to be around that and the variation is going to be given by b_1E_{ac}.

Here it is going to be little more complex you will write k_1 or k_2, I would write it as k_i here. k_i is going to vary around k_{idc}, but the variation is given by (1+ b_{1ac} E_{ac}) (1+ $\beta_1 g$(dθ/dE) E_{ac}). Whatever you have done for k_1 you can do for k_2. θ is not going to be special, we have seen this before it is going to be just θ_{SS} + dθ/dE E_{ac}.

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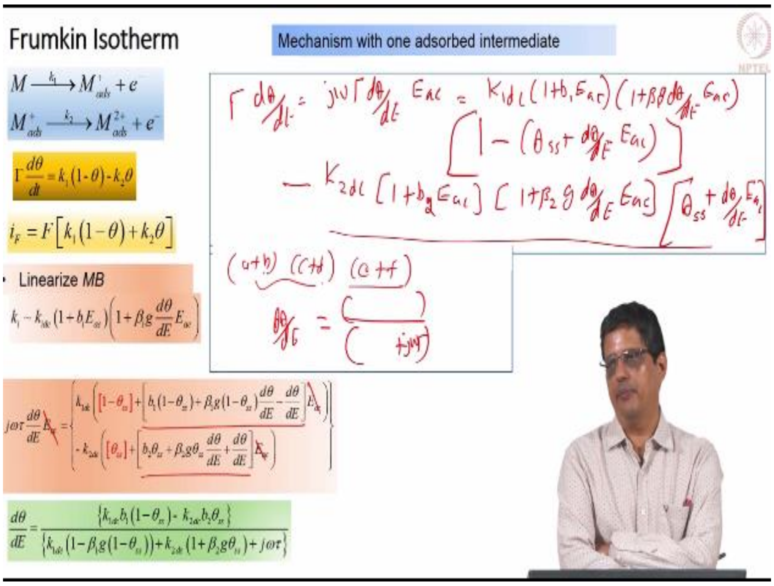

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$i_F = F\left[k_1(1-\theta) + k_2\theta\right]$

- Linearize *MB*

$k_1 \sim k_{1dc}(1+b_1E_{ac})\left(1+\beta_1 g \frac{d\theta}{dE}E_{ac}\right)$

$$j\omega\tau \frac{d\theta}{dE}\cancel{E_{ac}} = \left\{\begin{array}{l} k_{1dc}\left([1-\theta_{ss}] + \left[b_1(1-\theta_{ss}) + \beta_1 g(1-\theta_{ss})\frac{d\theta}{dE} - \frac{d\theta}{dE}\right]\cancel{E_{ac}}\right) \\ -k_{2dc}\left([\theta_{ss}] + \left[b_2\theta_{ss} + \beta_2 g\theta_{ss}\frac{d\theta}{dE} + \frac{d\theta}{dE}\right]\cancel{E_{ac}}\right) \end{array}\right\}$$

$$\frac{d\theta}{dE} = \frac{\{k_{1dc}b_1(1-\theta_{ss}) - k_{2dc}b_2\theta_{ss}\}}{\{k_{1dc}(1-\beta_1 g(1-\theta_{ss})) + k_{2dc}(1+\beta_2 g\theta_{ss}) + j\omega\tau\}}$$

$$\Gamma \frac{d\theta}{dt} = j\omega\Gamma\frac{d\theta}{dE}E_{ac} = K_{1dc}(1+b_1E_{ac})\left(1+\beta g\frac{d\theta}{dE}E_{ac}\right)\left[1-\left(\theta_{ss}+\frac{d\theta}{dE}E_{ac}\right)\right]$$
$$- K_{2dc}\left[1+b_2E_{ac}\right]\left[1+\beta_2 g\frac{d\theta}{dE}E_{ac}\right]\left[\theta_{ss}+\frac{d\theta}{dE}E_{ac}\right]$$

$(a+b)\ (c+d)\ (e+f)$

$$\frac{d\theta}{dE} = \frac{(\quad)}{(\quad + j\omega\tau)}$$

I would like you to write this equation, left hand side, it is going to be similar to what we have done before, right hand side it is going to be little more complex. See when we looked at catalytic mechanism, we found that it is a second order reaction in one of those steps that means k_1 will give rise to one E_{ac} term, θ will give rise to one E_{ac} term, (1–θ) will give rise to one E_{ac} term. And when you multiply this you will get up to cubic level, but we are going to anyway truncate it first order therefore we will neglect E_{ac}^2, E_{ac}^3, we have to do the same thing here. k_1 here gives rise to two E_{ac} terms here. The product will get 4 terms in the k_1, but I will retain only three terms. Right now, I am just keeping them as they are. θ will give rise to one more E_{ac}. (**"Professor - student conversation starts"** Sir 1- θ. Thank you. **"Professor - student conversation ends"**)

k_2 is going to be approximated as k_{2dc}, b_2 E_{ac} is going to be there, (1+ β_2g (dθ/dE)E_{ac}) is going to be there and this has to be multiplied by θ value. It is going to be θ_{SS} + dθ/dE E_{ac}. Each term will give rise to constant E_{ac}^2, E_{ac}^3. We are going to neglect E_{ac}^2 and E_{ac}^3. I would like you to write the constant values. And you will see that they will go to zero. E_{ac} terms will remain and we will cancel the E_{ac} [but please go through that and rearrange]. Maybe one thing that can help you is when you look at (1-θ), it is going to be 1-(θ_{SS} + (dθ/dE) E_{ac}) within bracket, keep (1- θ) as 1 term and then –(dθ/dE) E_{ac} as the second term. Because the (1- θ_{SS}) is the constant term for a given dc, -(dθ/dE) is the linear term as far as E_{ac} is concerned.

Sometimes in different notation when people write they will write 1-θ_{SS} as θ_{Vss}, θ vacant site. The first term as to give rise to what I have written here on the top and the second term towards written in the bottom assuming that I have done it correctly. See if you look at the second term here it is like (a + b), (c + d), (e + f), this b, d and f are linear functions of E_{ac}. The first number is a constant. θ_{SS} or 1. You are going to have 4 terms when you multiply this. You are going to have 8 terms when you multiply all the 3 terms there. Out of the 8 terms you will get a constant, you will get E_{ac}, you will get E_{ac}^2 and E_{ac}^3. Neglect or throwaway the E_{ac}^2 and E_{ac}^3 terms.

Once you get this, I have marked two terms in red colour. This correspond to the dc terms and they will go to zero because by definition of θ_{SS} it is k_{1dc} (1- θ_{SS}) has to be equal to k_{2dc} θ_{SS}, that is how we got the steady state values anyway. These terms will go away; remaining terms are those, which are left with E_{ac}. We can cancel out the E_{ac}s here, then you can bring dθ/dE terms to the left side the other terms will remain on the right side and you can get an expression for dθ/dE = something/something. The denominator will have jωΓ for sure. If necessary, copy these terms and then rearrange it. One-way to check that the expression you have got is to set the value of g to 0, if g is set to 0, it has to be Langmuir isotherm result. If you said β_1, β2 to 0 it should go to Langmuir isotherm result. Main point here is it may be lengthy, but it is quite doable. It is not very difficult in terms of how complex the problem is, it will be lengthy, it has many terms, but as long as you have enough time to go through it, verify it, it is actually straightforward. You have to do it slowly and with care that is all. You get an expression for dθ/dE, this we obtain by linearizing the mass balance equation. You can take the charge balance equation and linearize it here. We use k_i as k_{idc} (1+ b_iE_{ac}) and the next term for the Frumkin isotherm.

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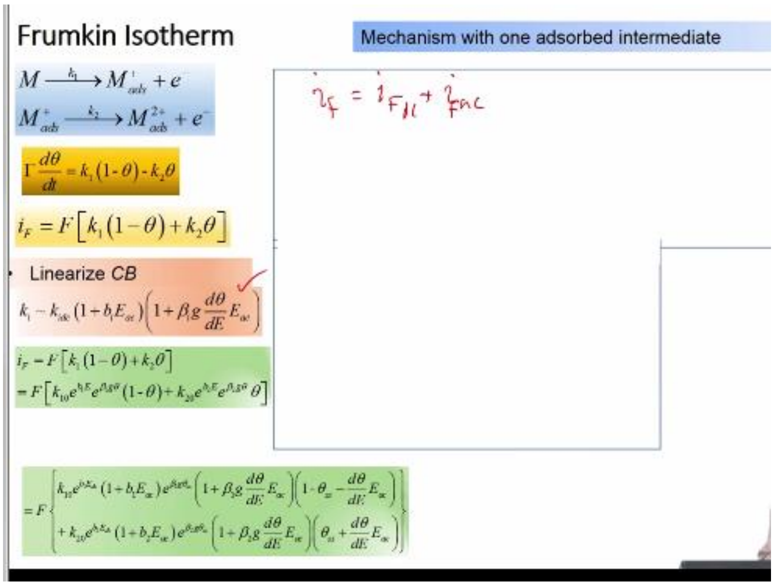

Frumkin Isotherm

Mechanism with one adsorbed intermediate

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

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

$$\Gamma \frac{d\theta}{dt} = k_1(1-\theta) - k_2\theta$$

$$i_F = F\left[k_1(1-\theta) + k_2\theta\right]$$

- Linearize CB

$$k_i - k_{idc}(1+b_iE_{ac})\left(1+\beta_i g\frac{d\theta}{dE}E_{ac}\right)$$

$$i_F = F\left[k_1(1-\theta)+k_2\theta\right]$$
$$= F\left[k_{10}e^{b_1E}e^{\beta_1 g\theta}(1-\theta)+k_{20}e^{b_2E}e^{\beta_2 g\theta}\,\theta\right]$$

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

$$= F\left\{\begin{aligned}&k_{10}e^{b_1E_{dc}}(1+b_1E_{ac})e^{\beta_1 g\theta_{ss}}\left(1+\beta_1 g\frac{d\theta}{dE}E_{ac}\right)\left(1-\theta_{ss}-\frac{d\theta}{dE}E_{ac}\right)\\&+k_{20}e^{b_2E_{dc}}(1+b_2E_{ac})e^{\beta_2 g\theta_{ss}}\left(1+\beta_2 g\frac{d\theta}{dE}E_{ac}\right)\left(\theta_{ss}+\frac{d\theta}{dE}E_{ac}\right)\end{aligned}\right\}$$

θ if we can substitute as θ_{SS}, this is actually fairly straightforward again. [It is again going to be little lengthy but may be know we are short of time so what I am going to do is to say that yes if you spend time you can expand this]. You will get a lengthy expression; you can substitute for dθ/dE from the previous case. Before you do that when you expand it, it is going to give rise to a steady state current and a ac current.

When you write this in terms of k_{1dc} and E_{ac} θ_{SS} and $d\theta/dE_{ac}$, you can group all the constant terms together. You can show that they are corresponding to i_{Fdc}, Faradaic current, constant terms will come like this, and the E_{ac} terms will come like this i_{Fac}, we are going to, of course, neglect E_{ac} square and other higher order terms.

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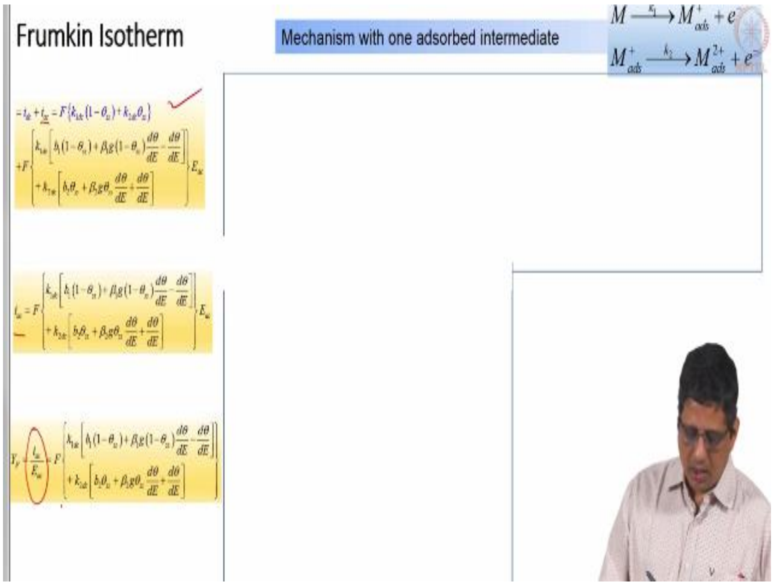

Frumkin Isotherm

Mechanism with one adsorbed intermediate

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

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

$$= i_{dc} + i_{ac} = F\{k_{1dc}(1-\theta_{ss}) + k_{2dc}\theta_{ss}\} + F\left\{\begin{array}{l} k_{1dc}\left[b_1(1-\theta_{ss}) + \beta_1 g(1-\theta_{ss})\frac{d\theta}{dE} - \frac{d\theta}{dE}\right] \\ + k_{2dc}\left[b_2\theta_{ss} + \beta_2 g\theta_{ss}\frac{d\theta}{dE} + \frac{d\theta}{dE}\right]\end{array}\right\} E_{ac}$$

$$i_{ac} = F\left\{\begin{array}{l} k_{1dc}\left[b_1(1-\theta_{ss}) + \beta_1 g(1-\theta_{ss})\frac{d\theta}{dE} - \frac{d\theta}{dE}\right] \\ + k_{2dc}\left[b_2\theta_{ss} + \beta_2 g\theta_{ss}\frac{d\theta}{dE} + \frac{d\theta}{dE}\right]\end{array}\right\} E_{ac}$$

$$Y_F = \frac{i_{ac}}{E_{ac}} = F\left\{\begin{array}{l} k_{1dc}\left[b_1(1-\theta_{ss}) + \beta_1 g(1-\theta_{ss})\frac{d\theta}{dE} - \frac{d\theta}{dE}\right] \\ + k_{2dc}\left[b_2\theta_{ss} + \beta_2 g\theta_{ss}\frac{d\theta}{dE} + \frac{d\theta}{dE}\right]\end{array}\right\}$$

So if you spend enough time, you can rearrange it, and take only the ac part that is going to come as proportional to E_{ac}, and write the ratio of i_{ac} to E_{ac} and call it as faradaic admittance. If you invert it, you will get faradaic impedance. Point here is if you write like this.

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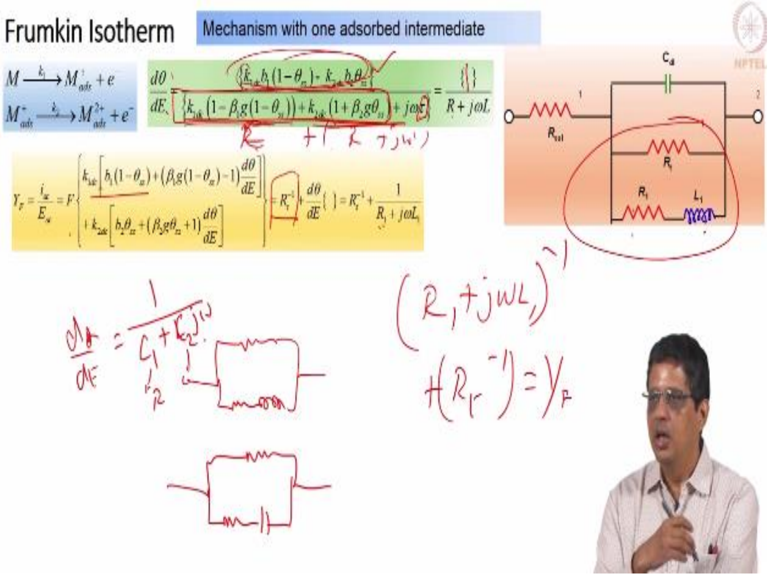

Frumkin Isotherm

Mechanism with one adsorbed intermediate

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

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

$$\frac{d\theta}{dE} = \frac{\{k_{1dc} b_1 (1-\theta_{ss}) - k_{2dc} b_2 \theta_{ss}\}}{\{k_{1dc}(1-\beta_1 g(1-\theta_{ss})) + k_{2dc}(1+\beta_2 g\theta_{ss}) + j\omega\Gamma\}} = \frac{\{\}}{R + j\omega L}$$

$$Y_F = \frac{i_{ac}}{E_{ac}} = F\left\{\begin{array}{l} k_{1dc}\left[b_1(1-\theta_{ss}) + (\beta_1 g(1-\theta_{ss}) - 1)\frac{d\theta}{dE}\right] \\ + k_{2dc}\left[b_2\theta_{ss} + (\beta_2 g\theta_{ss} + 1)\frac{d\theta}{dE}\right] \end{array}\right\} = R_t^{-1} + \frac{d\theta}{dE}\{\ \} = R_t^{-1} + \frac{1}{R_1 + j\omega L_1}$$

The faradaic impedance can be modelled using a circuit like this. That it has a resistance, this case I have written it as R_1 L_1 but we also know that any circuit that is given like this can be model by another circuit or any impedance that is coming from this circuit can be modelled by a circuit like this. It is just that here it is easy to relate to the L here. Otherwise it does not mean it has to be an inductance. It may be inductance with negative value for R_1 L_1; it may be an inductance with positive value for R_1 L_1. The reason is, you get dθ/dE and everything else is a constant here. (dθ/dE) is a function of ω. We have seen this before, dθ/dE comes as a function of ω, it is written like this but I can divide by the value here in the numerator and denominator. I am going to get k_{1dc} this divided by this entire term it is going to look like 1/some resistance + some other term + j ω something is not resistance, only some constant. These 3 terms can be written as resistance in parallel with resistance and inductance. Because what do you get here, you get impedance here as $R_1 + j\omega L_1$, that is going to be the impedance there. This is going to give you faradaic impedance. Faradaic impedance for this case or in general this is going to be the impedance or admittance of this circuit is going to be given by the inverse of this + inverse of this (refer video, 33:05).

Same form will come here when you look at it here. If I substitute for dθ/dE, ultimately what I would get is one constant here and some dθ/dE * some constant value parameter here, I can call this as $(R_t)^{-1}$ and this is going to be given as $1/(R_1+j\omega L)$. Because dθ/dE can be written as 1/R jωL. in fact I should say, all this put together should be the R value and j ω Γ by this term is going to be the L term. The point is I can write dθ/dE as 1/some constant + another constant * j ω. Some constant C_1 C_2 j ω. I can call this as R, I can call this as L, it does not matter. Ultimately, it is one adsorbed intermediate.

It is going to give rise to 1 Maxwell element, it does not matter whether it is Langmuir isotherm or Frumkin isotherm or Temkin isotherm. Of course, the values will differ depending on the rate constant values, but this reaction, depending on the values can give rise to a spectrum like.

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This it can give rise to a spectrum like this in the complex plane plot and if the values are such that they cancel out each other, it can give rise to only one. That is if dθ/dE is 0 because the numerator is 0, you will not have any impact from this R_1 L_1 parameters. The thing is it will give rise to one loop at the faradaic, because of the faradic contribution. It can be inductive or capacitive; it may not give rise to thing.

In fact, when you do experimentally it may give rise to these two loops but we may measure only in this frequency range, in which case you will see only one loop. However, this cannot give rise to loop like this; it cannot give rise to a loop like this. If it comes like this, you can say it is going to need 2 adsorbed intermediate to model this. Although the number of variable parameters.

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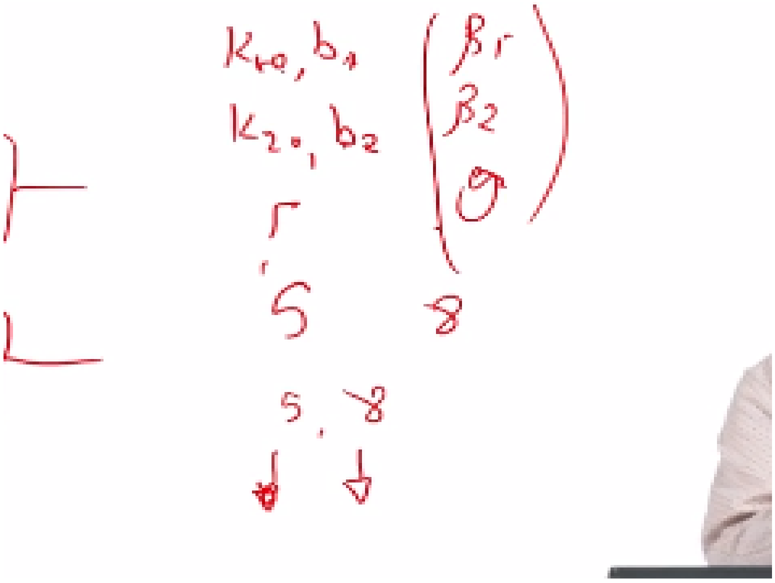

See previously in Langmuir isotherm model, k_{10}, b_1, k_{20}, b_2, Γ these are the kinetic parameters that you can vary in order to fit this model to a data set, you have 5 parameters. If you say I think this is following a Frumkin isotherm model, you are adding 3 more parameters; still it will give rise to only this. Five parameters in Langmuir, 8 parameters in Frumkin for equation, which looks the same, mass balance and charge balance equation look the same, it is just the kinetic parameters, the form of the kinetic parameters we are making it dependent on θ therefore it gives rise to this. But, if I want to get these things correctly I need to take spectrum at multiple dc potentials to get this because circuit wise it gives rise to 3 elements. Kinetic parameter wise I am taking either 5 element or 8 elements.

If I model with one E_{dc} if I take this, I will get infinite number of solutions. If I assume it is Langmuir isotherm with 2 E_{dc} I can have some confidence, if I assume it is Frumkin isotherm I need minimum of 3 dc potentials in order to get the values of these parameters with some confidence. I will come to that later, it is precise way of doing this, but this is to say it is possible to do it, it is lengthy, but it is possible to do it. And at the top level to know how many loops I can get or what kind of mechanism I should use to model a adsorbed spectrum or model a multiple spectra, you need to count the time constant there. Except for the high frequency impedance, which comes from double layer, everything else, the total number of time constant you get tells you the total number of immediate species, regardless of whether we say it is following Langmuir isotherm or more complicated isotherm.

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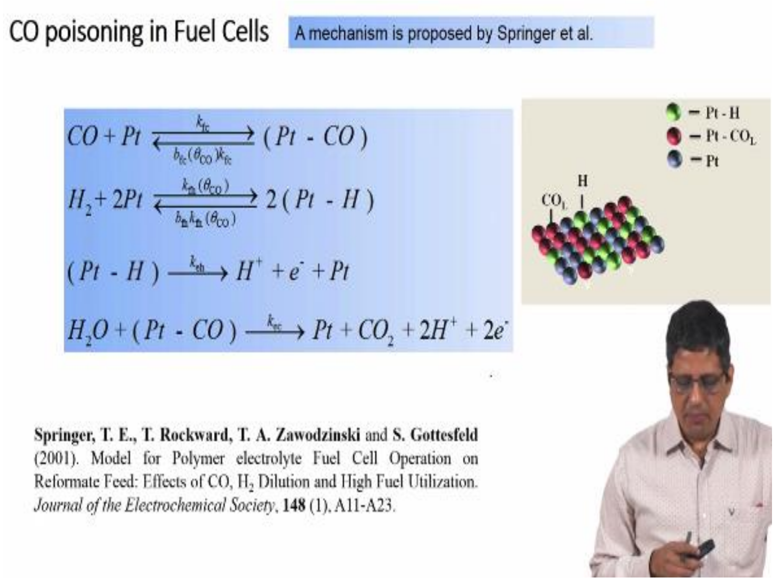

CO poisoning in Fuel Cells

A mechanism is proposed by Springer et al.

$$CO + Pt \underset{b_{fc}(\theta_{CO})k_{fc}}{\overset{k_{fc}}{\rightleftarrows}} (Pt - CO)$$

$$H_2 + 2Pt \underset{b_{fh}k_{fh}(\theta_{CO})}{\overset{k_{fh}(\theta_{CO})}{\rightleftarrows}} 2(Pt - H)$$

$$(Pt - H) \xrightarrow{k_{eh}} H^+ + e^- + Pt$$

$$H_2O + (Pt - CO) \xrightarrow{k_{ec}} Pt + CO_2 + 2H^+ + 2e^-$$

Springer, T. E., T. Rockward, T. A. Zawodzinski and S. Gottesfeld (2001). Model for Polymer electrolyte Fuel Cell Operation on Reformate Feed: Effects of CO, H_2 Dilution and High Fuel Utilization. *Journal of the Electrochemical Society*, **148** (1), A11-A23.

[I think I am going to skip this, you have lot more complex mechanism that is proposed here and a lot more complex dependency].

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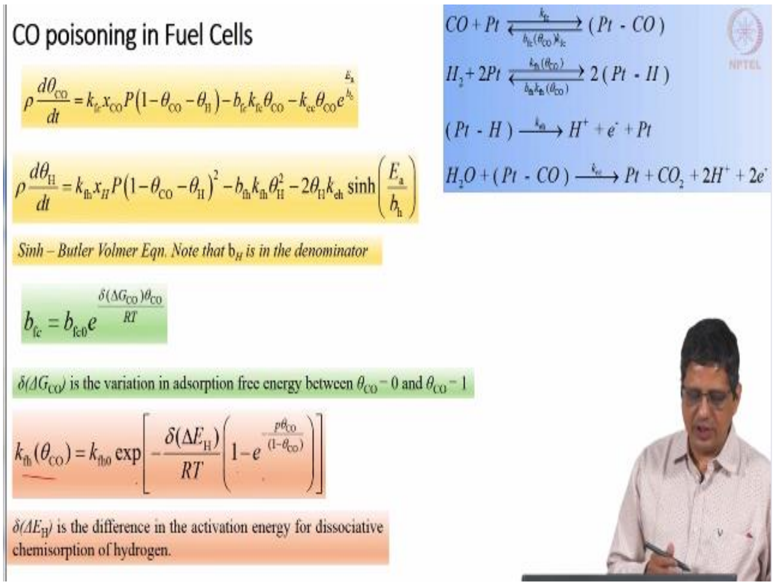

CO poisoning in Fuel Cells

$$\rho \frac{d\theta_{CO}}{dt} = k_{fc} x_{CO} P(1-\theta_{CO}-\theta_H) - b_{fc} k_{fc} \theta_{CO} - k_{ec} \theta_{CO} e^{\frac{E_a}{b_c}}$$

$$\rho \frac{d\theta_H}{dt} = k_{fh} x_H P(1-\theta_{CO}-\theta_H)^2 - b_{fh} k_{fh} \theta_H^2 - 2\theta_H k_{eh} \sinh\left(\frac{E_a}{b_h}\right)$$

Sinh – Butler Volmer Eqn. Note that b_H *is in the denominator*

$$b_{fc} = b_{fc0} e^{\frac{\delta(\Delta G_{CO})\theta_{CO}}{RT}}$$

$\delta(\Delta G_{CO})$ is the variation in adsorption free energy between $\theta_{CO} = 0$ and $\theta_{CO} = 1$

$$k_{fh}(\theta_{CO}) = k_{fh0} \exp\left[-\frac{\delta(\Delta E_H)}{RT}\left(1 - e^{\frac{p\theta_{CO}}{(1-\theta_{CO})}}\right)\right]$$

$\delta(\Delta E_H)$ is the difference in the activation energy for dissociative chemisorption of hydrogen.

$$CO + Pt \underset{b_{fc}(\theta_{CO})k_{fc}}{\overset{k_{fc}}{\rightleftarrows}} (Pt - CO)$$

$$H_2 + 2Pt \underset{b_{fh}k_{fh}(\theta_{CO})}{\overset{k_{fh}(\theta_{CO})}{\rightleftarrows}} 2(Pt - H)$$

$$(Pt - H) \xrightarrow{k_{eh}} H^+ + e^- + Pt$$

$$H_2O + (Pt - CO) \xrightarrow{k_{ec}} Pt + CO_2 + 2H^+ + 2e^-$$

Where one of the rate constant is given in terms of exponential of something, within that exponent you have 1 - exponential of something, and that exponent is θ/1- θ. [No problem, it is going to take time and few pages, but you can linearize this and I show in example of how to linearize this]. First, you take θ as, θ_{SS} + dθ/dE E_{ac}. Then keep all the components that are dc in one group anything with E_{ac} in another group. If it is exponential, keep it as the small number, you can write e^x as 1+ x, rearrange, it is again exponential no problem, rearrange, θ/1- θ you can expand and rearrange.

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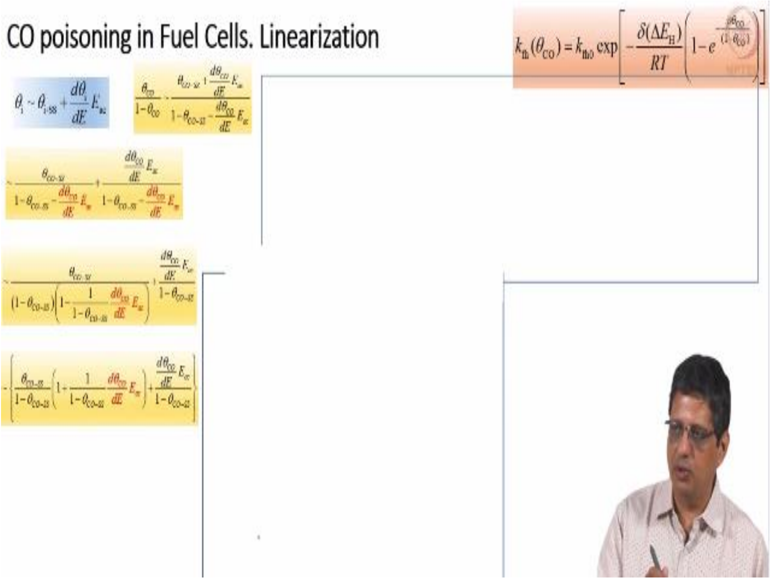

CO poisoning in Fuel Cells. Linearization

$$k_{fh}(\theta_{CO}) = k_{fh0}\exp\left[-\frac{\delta(\Delta E_H)}{RT}\left(1-e^{-\frac{p\theta_{CO}}{(1-\theta_{CO})}}\right)\right]$$

$$\theta_i \sim \theta_{i\text{-}ss} + \frac{d\theta_i}{dE}E_{ac}$$

$$\frac{\theta_{CO}}{1-\theta_{CO}} \sim \frac{\theta_{CO\text{-}ss} + \frac{d\theta_{CO}}{dE}E_{ac}}{1-\theta_{CO\text{-}ss} - \frac{d\theta_{CO}}{dE}E_{ac}}$$

$$\sim \frac{\theta_{CO\text{-}ss}}{1-\theta_{CO\text{-}ss}-\frac{d\theta_{CO}}{dE}E_{ac}} + \frac{\frac{d\theta_{CO}}{dE}E_{ac}}{1-\theta_{CO\text{-}ss}-\frac{d\theta_{CO}}{dE}E_{ac}}$$

$$\sim \frac{\theta_{CO\text{-}ss}}{(1-\theta_{CO\text{-}ss})\left(1-\frac{1}{1-\theta_{CO\text{-}ss}}\frac{d\theta_{CO}}{dE}E_{ac}\right)} + \frac{\frac{d\theta_{CO}}{dE}E_{ac}}{1-\theta_{CO\text{-}ss}}$$

$$\sim \left\{\frac{\theta_{CO\text{-}ss}}{1-\theta_{CO\text{-}ss}}\left(1+\frac{1}{1-\theta_{CO\text{-}ss}}\frac{d\theta_{CO}}{dE}E_{ac}\right) + \frac{\frac{d\theta_{CO}}{dE}E_{ac}}{1-\theta_{CO\text{-}ss}}\right\}$$

[θ /1- θ, right now I am not going to go through, but I want to just show you it is possible to do it and you can see the description in the file].

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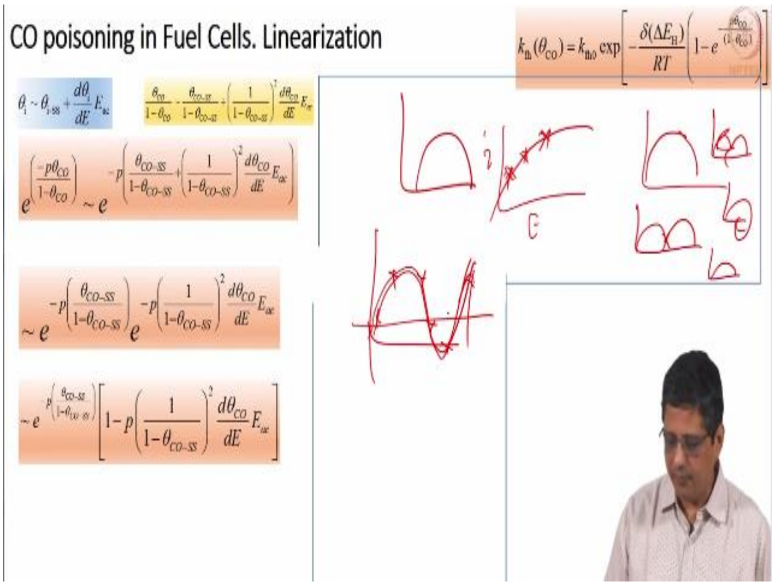

CO poisoning in Fuel Cells. Linearization

$$k_{fh}(\theta_{CO}) = k_{fh0}\exp\left[-\frac{\delta(\Delta E_H)}{RT}\left(1-e^{-\frac{p\theta_{CO}}{(1-\theta_{CO})}}\right)\right]$$

$$\theta_i \sim \theta_{i\text{-}ss} + \frac{d\theta_i}{dE}E_{ac}$$

$$\frac{\theta_{CO}}{1-\theta_{CO}} \sim \frac{\theta_{CO\text{-}ss}}{1-\theta_{CO\text{-}ss}} + \left(\frac{1}{1-\theta_{CO\text{-}ss}}\right)^2\frac{d\theta_{CO}}{dE}E_{ac}$$

$$e^{\left(\frac{-p\theta_{CO}}{1-\theta_{CO}}\right)} \sim e^{-p\left(\frac{\theta_{CO\text{-}ss}}{1-\theta_{CO\text{-}ss}} + \left(\frac{1}{1-\theta_{CO\text{-}ss}}\right)^2\frac{d\theta_{CO}}{dE}E_{ac}\right)}$$

$$\sim e^{-p\left(\frac{\theta_{CO\text{-}ss}}{1-\theta_{CO\text{-}ss}}\right)} e^{-p\left(\frac{1}{1-\theta_{CO\text{-}ss}}\right)^2\frac{d\theta_{CO}}{dE}E_{ac}}$$

$$\sim e^{-p\left(\frac{\theta_{CO\text{-}ss}}{1-\theta_{CO\text{-}ss}}\right)}\left[1-p\left(\frac{1}{1-\theta_{CO\text{-}ss}}\right)^2\frac{d\theta_{CO}}{dE}E_{ac}\right]$$

It is possible to rearrange and get it. Finally, you can get expression for dθ/dE, you can get an expression for i_{Fac} in terms of E_{ac}, and you can get faradaic impedance out of this. It is going to be very lengthy, so lot of times you end up using intermediate variables to describe certain quantities. [Tomorrow what I want to show you is, describe some of the challenges faced when you actually have data and you want to get model].

So far what we have seen is, if you are given a model can we write an expression for faradaic impedance? We also at a superficial level see that if you are given a spectrum or few spectra we should say this mechanism would never model this because this has 5 loops and mechanism has only 2 intermediates, or this has 2 loops and my mechanism has only one intermediate. This cannot model I need to have a mechanism, propose a mechanism with 2 intermediates or 3 intermediates that much we know, but what else do we have to really do to get this [that we will see tomorrow]. (**“Professor - student conversation starts”** Sir the number of loops is equal to the number of intermediates? Number of loops, high-frequency loop you will get because of double layer capacitance and a charge transfer resistance. **“Professor - student conversation ends”**)

That means, in a simple electron transfer reaction with no intermediates you get a curve, which looks like this. Anything else in addition to this how many loops do we have? It does not mean those are the number of intermediates, it means minimum that many intermediates you need. Let us say I have a data where potentiodynamic polarization i versus E shows a curve like this.

I take spectrum here, spectrum here, spectrum here and I am going to take it in a finite frequency range. Some number right, maybe 1 mHz, may be 1 μHz. [I do not think we have instrument with 1 μHz. We can go from 10 mHz, 10 μHz to 10 kHz, 100 kHz]. It is possible that it shows a spectrum like this at this potential. At this potential, it may show a spectrum like this. This potential it may show a spectrum like this or it may show a spectrum like this. It may show a spectrum like this. Then I say other than this high frequency loop, I have one more loop either inductive or capacitive. I have to look at all the spectra, find the maximum number of loops in those and then say, that many intermediate species is necessary to describe this. It is possible that when you try this mechanism it may fit or may not fit.

You can try similar mechanisms with same number of intermediate species and see if it can fit. If it does not fit, you may have to go to another more complex mechanism. Minimum number of intermediates is necessary to describe this can be obtained by looking at the number of loops there. It is like saying I have data like this, I know I cannot fit it linearly, but do I need cubic equation, do you need quadratic equation, do you need fourth power, I have to try that and see. Minimum I need quadratic, that visually you can see that and tell, but here you can tell minimum what you need is dependent on the number of loops. If I have a data like this, I cannot do a quadratic. That much I can tell. It may actually be sinusoidal that is a different story, but in this range I have taken data it looks like this, I want to model with something that can do this. I have data points 1, 2, 3, 4, 5, 6 data points.

It may actually not fit with the cubic. You might need a fourth order, fifth order, but at least cubic is something you should try. Spending our time on linear equation and quadratic equation is a waste of time. It is not going to be dependent on the algorithm we use or initial points we choose; it is never going to fit. Cubic is something where you should spend time because it has 1 minimum and 1 maximum. You know quadratic can represent this. Cubic can give you 3 roots, real roots, imaginary roots that is a different story, if I differentiates it is going to give me a quadratic equation that means it is going to show me 2 zeros. That means I can model one minimum, one maximum. It is a possibility. I should try with a cubic equation.

If it does not work, I should see if my algorithm is good. If I am convinced. I have done my best, I am not able to fit with cubic, I have to go to fourth order. Likewise, you can choose minimum number of adsorbed intermediates by looking at all the spectra and then the same number of adsorbed intermediates you may have multiple mechanisms. There are infinite number of mechanisms one can propose. You propose few reasonable whatever appears to be reasonable based on whatever evidence you have from other information. For example, if it is iron going to Fe going to Fe^{3+}, I will propose Fe^{2+} and Fe^{3+} as intermediates because these are stable. Fe^{1+} is not known to be a stable intermediate. I am going to come up with 2 intermediates, it is going to be 2+ and 3+, not 1+ and 2+ or 1+ and 3+.

This information comes from outside, not from the impedance spectrum because I know something about this system. If it is going to be titanium, I am going to say 3+ and 4+. Just by looking at the spectrum, I cannot tell everything about this. I have to have some information about the system. [We will stop here today].