Electrochemical Impedance Spectroscopy
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Lecture – 40
Applications

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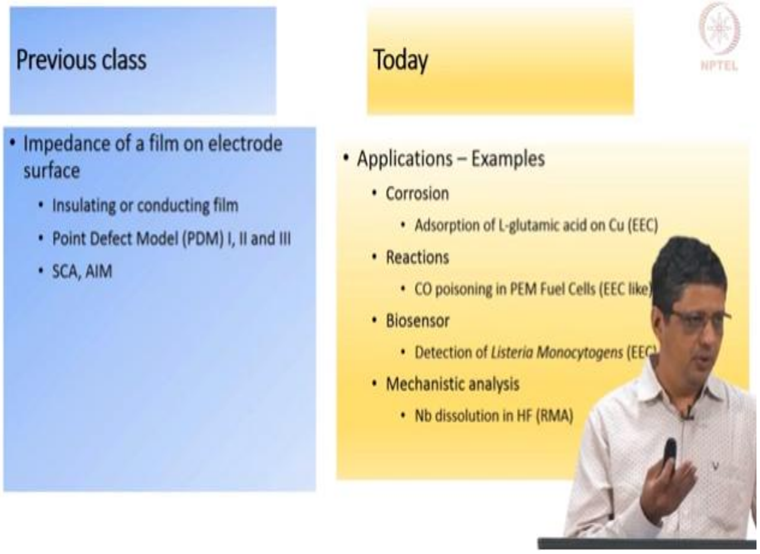

Previous class

- Impedance of a film on electrode surface
  - Insulating or conducting film
  - Point Defect Model (PDM) I, II and III
  - SCA, AIM

Today

- Applications – Examples
  - Corrosion
    - Adsorption of L-glutamic acid on Cu (EEC)
  - Reactions
    - CO poisoning in PEM Fuel Cells (EEC like)
  - Biosensor
    - Detection of *Listeria Monocytogens* (EEC
  - Mechanistic analysis
    - Nb dissolution in HF (RMA)

In the last class we have seen different models for describing the impedance of a film. What I want to show you today is, few example applications. How the impedance spectra have been analysed and used in the literature. I want to describe four examples two of them from our group and two of them from research in other labs. First example is on corrosion where basically we use electrically equivalent circuit.

The second example is on CO, carbon monoxide poisoning in fuel cells and that uses basically EEC. The third example is on biosensor and that uses EEC. The last example is from our group which is using mechanistic analysis. Most of the literature if you see they would use equivalent circuit. Because its lot easier to work with. A lot easier to fit a model for the given data. Interpretation making sense out of it sometimes it's easy sometimes it is not so easy.

In RMA, the analysis part is challenging so you do not see that many publications with mechanistic analysis. The first example is measurement of, or quantification of adsorption of an organic chemical called L-glutamic acid on copper electrode in nitric acid solution.

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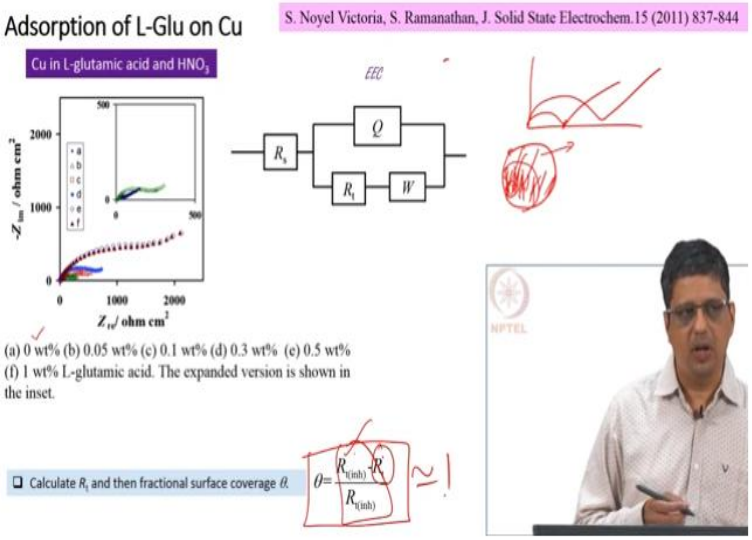

Adsorption of L-Glu on Cu

S. Noyel Victoria, S. Ramanathan, J. Solid State Electrochem.15 (2011) 837-844

Cu in L-glutamic acid and HNO_3

(a) 0 wt% (b) 0.05 wt% (c) 0.1 wt% (d) 0.3 wt% (e) 0.5 wt% (f) 1 wt% L-glutamic acid. The expanded version is shown in the inset.

☐ Calculate R_t and then fractional surface coverage θ.

$$\theta = \frac{R_{t(inh)} - R_t}{R_{t(inh)}} \simeq 1$$

In nitric acid solution copper will dissolve but if the organic chemicals we put in if it adsorbs on the surface, it can block or reduce the interaction between the nitric acid and copper. That basically acts as a corrosion inhibitor although the not necessarily the purpose for which it was used in that literature. So, what is done here is, copper electrode in nitric acid at open circuit condition, take impedance spectrum. And that is given by the figure. That is given in the insert you see in the insert there are two plots. These are complex plane plots. The blue colour plot actually shows a small semicircle and a 45° line. It is not very clear the small semi circle is not very clear what if we zoom in you would not be able to see. That corresponds to 0 weight % that means no additive no corrosion inhibitor.

If you use a small quantity 0.05 weight % of corrosion inhibitor, you see another semicircle in the green colour semicircle followed with a 45° line. And you can see the impedance values are larger and both are in the inset. Third one is for the little higher quantity. And that is the red colour in the main figure C. Fourth one is 0.3 weight% that is blue diamonds D and the fifth one is 0.58% which is a blue circle open circle.

Sixth one is more or less same as the fifth one. The weight% is higher but the impedance spectrum is similar to what you see for the fifth one. So, this is the spectrum that is obtained. Analysis is basically using following circuit. R_t is the charge transfer resistance R_s is solution resistance and instead of double layer capacitor, it is modeled with a constant physical element (CPE), and Warburg element because these experiments were done without rotation, stationary electrodes solution was unstirred and in addition you can also see the 45° line at the low frequencies. So, when you fit this, (I am not showing you the fits) it fits and you can get values. Solution resistance will be more or less the same. Because small amounts of this chemical is not going to change the solution resistance significantly. R_t value will increase, meaning the semicircle diameter will keep increasing when I add more and more of this chemical. And there is a way to quantify that. Here I have shown you in weight % for the L glutamic acid. The next slide actually you have calculated using concentration in molars and millimolar.

After we get R_t we calculate a quantity called surface coverage. The way we visualise is let's say this is the area of the electrode if we say that we had a small quantity of the inhibitor it can go and cover the surface. We add larger quantity of course some of it will go and adsorb and the adsorb species will come out sometimes. So, it is going to be under steady state condition. If you have more concentration in the liquidity more lately the surface coverage is larger. When surface coverage is larger we say that only the remaining area is available for the actual reaction. So, the way we define surface coverage here is or the way we extracted is, if we say that with the inhibitor we get a R_t, without the incubator that is a 0 wt% we get a charge transfer resistance. We can estimate the surface coverage using this formula. When R_t inhibitor is same as R_t, you will get a 0 coverage. When R_t inhibitor is very very high that means if the entire surface is covered with this inhibitor charge transfer resistance will tend towards infinity its not going to be infinity, but it is going to be a large number, which case we are going to say this number is much larger than R_t. Therefore this will look ~ 1. So, from the R_t value, we estimate the surface coverage value. From the R_t value of this electrode with inhibitor and without inhibitor we estimate this surface coverage because we expect this to be just a physical process of adsorption and blocking.

So, it is effectively reducing the area of the electrode available for the reaction. That is how that reduces the net corrosion right and that is how we visualize this process.

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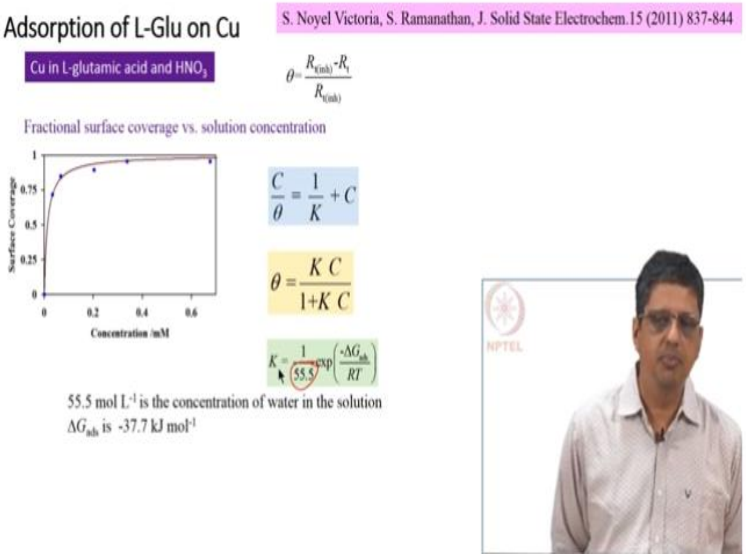

Adsorption of L-Glu on Cu

Cu in L-glutamic acid and HNO_3

S. Noyel Victoria, S. Ramanathan, J. Solid State Electrochem.15 (2011) 837-844

$$\theta = \frac{R_{t(inh)} - R_t}{R_{t(inh)}}$$

Fractional surface coverage vs. solution concentration

$$\frac{C}{\theta} = \frac{1}{K} + C$$

$$\theta = \frac{K\,C}{1 + K\,C}$$

$$K = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}}{RT}\right)$$

55.5 mol L^{-1} is the concentration of water in the solution

ΔG_{ads} is -37.7 kJ mol^{-1}

If you plot the fractional surface coverage as a function of concentration in the liquid, curve we get looks like this. At 0 concentration of course you will get 0 surface coverage and it increases quickly and then it more or less saturates which gives us the idea that it is probably described by Langmuir isotherm. Langmuir isotherm is described by this equation where C is the concentration in liquid, θ is the surface coverage of the same species. Usually people will rearrange it and say this is going to be described by a linear equation. And it is easier to verify it. But then now you have enough number of software tools that you can use this actual equation and nonlinear fit. That is actually a better description than getting this because you want to minimize the error in θ experimental and θ model you want to minimize this setup here? What it does is it minimizes the error of C/θ.

And that means there is going to be a difference in the value of 'k' that you get that is going to be a difference in the confidence value that you get. So, just to say that just because previous literature shows you this formula and says they minimise based on this does not mean you will have to do it that way. Now that we have access to easy nonlinear fit tools its better to use the actual equation and fit it.

And when you fit it you would get the value for K and that K is related to the ΔG value. 55.5 is actually the concentration of water in solution basically it is pretty much water. And ΔG you can get it using this formula. This is not the best way if you really want to get it correctly you will have to do it at various temperatures and then see if the K really follows this equation if I vary the temperature what happens here. But then, what we got is with 1 value 1 temperature. So we basically said we can describe this adsorption we wanted to show that this material adsorbs onto this surface we were able to show by saying that the impedance value increases and then were also able to quantify a little better.

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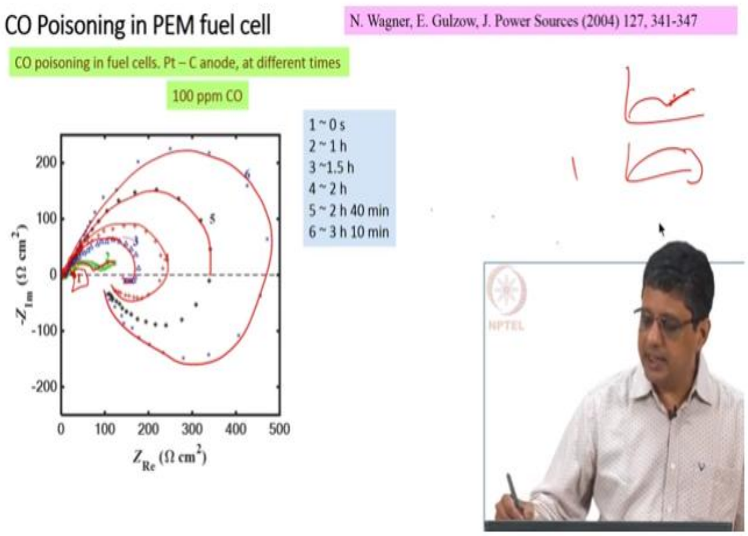

CO Poisoning in PEM fuel cell

N. Wagner, E. Gulzow, J. Power Sources (2004) 127, 341-347

CO poisoning in fuel cells. Pt – C anode, at different times

100 ppm CO

1 ~ 0 s
2 ~ 1 h
3 ~ 1.5 h
4 ~ 2 h
5 ~ 2 h 40 min
6 ~ 3 h 10 min

Second example is a fuel cell. In a fuel cell you have hydrogen this is the overall reaction. In the hydrogen fuel cell what you have is hydrogen splitting to form H^+ on one side, oxygen not just oxygen directly reacting with hydrogen or H^+ it is going to combine with water and form OH^- ions and they will react with H^+ ion and form water. So, on one side anode side in this fuel cell the anode side is where this happens. Cathode side is where oxygen reduction happens. On the anode side you have H^+, electron comes through the load whatever load we give and then comes to the cathode side there oxygen along with the electron and the water molecule forms OH^- and the hydrogen formed on the anode side moves through this combines with OH^- and forms water. This will give you 4 I am sorry $2H_2$ will give you 4 H^+ and 4 e-.

So, net reaction will still be $2H_2 + O_2$, although water is necessary to actually conduct this reaction. Here H^+ ion moves through this. There are other scenarios where OH^- will move through this alkaline fuel cell it can happen but the movement occurs because of the OH^- ion we are not going to worry about that hydrogen is produced usually from natural gas. So, it is from CH_4 it is suppose to give you CO_2 and H_2, but a small amount of CO may sneak through so that is causing CO poisoning. Oxygen is actually just air. We do not supply oxygen we usually supply air. Now this study was done in the following manner. In an actual fuel cell so you will have oxygen along with moisture control level going through one side hydrogen coming through the other side with the appropriate catalysts.

And then you will have the energy produced or electrons coming over through this. Here what they have done is they sealed this. That means it is pressurized with hydrogen but it is not flowing. Oxygen of course flows on this side. CO is not a good gas anyway. So you do not want to pump it and release it. And it is not easier to maintain the concentration if you are actually blocking it.

What they have done is taken the spectrum before poisoning so that is actually a small semicircle here. It is not very clear but it is a dark brown line indicated by this number 1. It is very small so you cannot see it here in this scale. After giving small amount of CO poisoning after an hour, looks like this. After hour and a half, actually two semicircles are merged together and then in addition you have an inductive loop. Initially it looks like this, second this loop becomes larger and larger that it actually becomes like 1 semi circle. It is not a semicircle really it is actually 2 semi circles combined. Comes like this you can see it is not really a semicircle right. It is not even distorted semicircle. It is not depressed semicircle where it just push down. It is actually you can actually visualise this as 2 semicircles merge together one is the smaller semicircle.

Another is changing with time. Initially it was small later it was larger later it was even larger therefore it looks like a distorted semicircle. And at even later time it goes like this. Looking at this, you can definitely say mid and low frequency impedance increases over time that means the process of poisoning is continuing it is a fixed concentration of CO but it has not come to a steady state yet over time it keeps increasing. Of course when CO poisoning happens in real cell what will happen is you will not be able to produce that much current. The efficiency of the catalyst will go down. But this is just a study to understand whether you can get a signature out of this.

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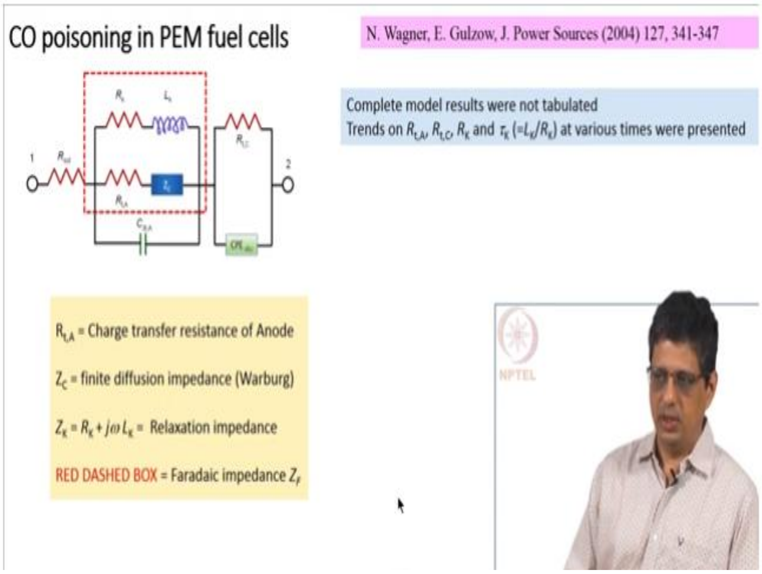

CO poisoning in PEM fuel cells

N. Wagner, E. Gulzow, J. Power Sources (2004) 127, 341-347

Complete model results were not tabulated
Trends on $R_{t,A}$, $R_{t,C}$, R_K and τ_K ($=L_K/R_K$) at various times were presented

$R_{t,A}$ = Charge transfer resistance of Anode

Z_C = finite diffusion impedance (Warburg)

$Z_K = R_K + j\omega L_K$ = Relaxation impedance

RED DASHED BOX = Faradaic impedance Z_F

Analysis is done with the following circuit. You have cathode to represent the oxygen reaction. They have represented that using a simple reaction, simple resistance, and a constant phase element. In between cathode and anode you have a membrane resistance. I am denoting that as a solution resistance here basically a simple resistor. And on the other side you have anode of course when you have cathode, membrane, and anode, and if you assume they are three distinct elements it does not matter whether I mix it this way or whether they put it in lined up like this. So, I have put cathode here anode here and then the membrane resistance it is going to give me the same impedance anyway. I have actually copied from the diagram I have just drawn it on my own but I followed the same sequence. Now, in the anode side for the double layer can be modeled using simple capacitor.

This whatever is shown in the red dashed box that is supposed to represent all the processes occurring there, faradaic process. That is denoted with one charge transfer resistance of the anode. Second, Warburg impedance, finite diffusion impedance. Third, they also use a pair of R and L Maxwell element but with the inductor and they denote that by something called relaxation impedance.

At this stage I want to make some remarks. First this system is modeled using a cathode with a resistor and a constant phase element. On the anode side it is modelled with a Maxwell element and a finite Warburg impedance or bounded Warburg impedance is added to that. Ideally what would we want to do? First of all, the oxygen reduction reaction is not a simple electron transfer reaction. It goes through multiple steps so it is a fairly complex reaction. On the anode side we have 2 reactions, 1 is hydrogen oxidation another is carbon monoxide oxidation.

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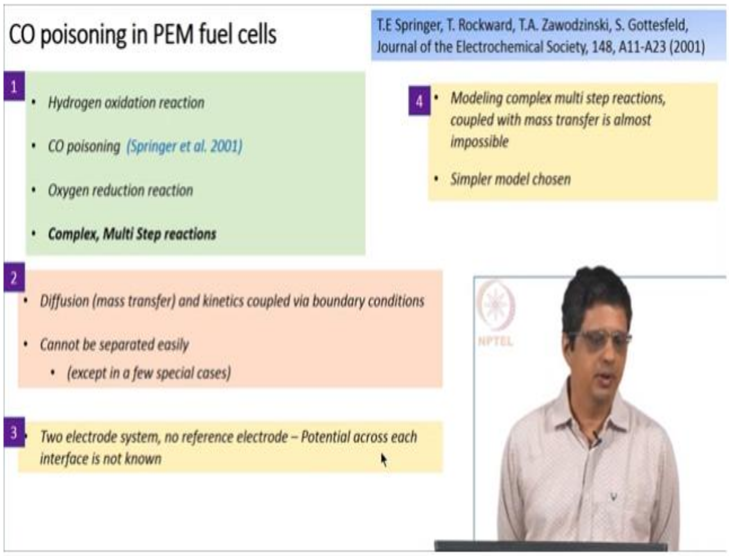

CO poisoning in PEM fuel cells

T.E Springer, T. Rockward, T.A. Zawodzinski, S. Gottesfeld, Journal of the Electrochemical Society, 148, A11-A23 (2001)

1
- *Hydrogen oxidation reaction*
- *CO poisoning (Springer et al. 2001)*
- *Oxygen reduction reaction*
- ***Complex, Multi Step reactions***

2
- *Diffusion (mass transfer) and kinetics coupled via boundary conditions*
- *Cannot be separated easily*
  - *(except in a few special cases)*

3
- *Two electrode system, no reference electrode – Potential across each interface is not known*

4
- *Modeling complex multi step reactions, coupled with mass transfer is almost impossible*
- *Simpler model chosen*

So, hydrogen oxidation reaction also does not happen with a single step it happens with multiple steps. There are studies exclusively for this hydrogen oxidation reactions. And at least you need one adsorbed intermediate to describe this reaction and carbon monoxide poisoning. The way it occurs is carbon monoxide adsorbs onto the catalyst surface and then it gets oxidised very slowly. So, essentially it adsorbs unblocks the catalyst surface and that is how it poisons and that will need at least one adsorbed intermediate. So, we will need 2 adsorb intermediate to describe the reactions in the anode side and we will need one adsorbed intermediate at least 1 adsorbed intermediate on the cathode side. So, it is actually complex multistep reactions this is just a pictorial of what one would expect to see.

Carbon monoxide can bind possibly in one side or can possibly on two sides. These are called linear or bridge mechanisms but this is how people have described this and ideally we would want to use some mechanisms either proposed in the literature or something that one can propose ourselves. We can propose ourselves and use that to describe the system. Not just that when you want to include mass transfer effect, and if you know that mass transfer effects are important. You cannot normally add Warburg impedance to the faradaic components that is obtained assuming mass transfer is rapid. Because diffusion and kinetics are coupled via boundary conditions, and in the simplest case that is simple electron transfer reaction, at open circuit potential one can write nicely separated expressions one for the charge transfer kinetics and another for the mass transfer.

But in general we have not derived any expression for complex reactions with mass transfer limitations. We just mentioned that it is possible but its actually extremely difficult. And it is not easy to separate but right now what is done is that you have possibly one adsorbed intermediate that is described by the charge transfer resistance along with the Maxwell couple that is denoted by Rk and Lk. And then mass transfer impedance is added as ZC or ZW bounded Warburg impedance.

The third point is ideally I would like to conduct an experiment with three electrode system with one electrode as the reference electrode and the potential should be measured with respect to the reference electrode. But then because of challenges involved in conducting such experiments in a fuel cell, 2 electrode system is used. Which means it is somewhat difficult to tell what the potential drop is across each electrode. What is the potential drop across anode and what is the potential drop across cathode? Still the authors have modelled in this fashion mainly because it is not that easy to even develop an expression for complex reactions even on only one side even on the anode side with mass transfer limitation. When you realized that you had to add the reactions on the cathode side also to calculate the total impedance it becomes next to impossible. Even as of today in 2018, if you develop the expression it might be possible for us to generate the spectrum for a given kinetic parameters and diffusivity parameter. But it is practically impossible to run it through an optimization program and fit and obtain the parameters.

To make sense out of the data and to get an understanding I would guess the authors have described this reaction on the anode side with a 1 absorbed intermediate species as a simplification. And then added the bounded Warburg impedance, added the diffusivity part to this. And that is how they have modelled this data. how do you know that you are supposed to introduce a Warburg impedance, in the first place.

Basically if you say that the mass transfer effect is playing a role you have to introduce. You cannot introduce a Warburg element that is my argument here but you have to account for mass transfer by some means. But you see the EIS spectrum and then you decide right? So EIS spectrum is one, second if you think the diffusion of the species is going to play a role because if you put a thicker membrane it is going to make an impact. You put a thicker catalysts layer [a gas diffusion layer] it is going to make an impact, then mass transfer is playing a role. So, you cannot just look at the spectrum all the time and say this is what is happening. I can look at the spectrum here and I can say it is probably Warburg impedance. But that is also because I know the solution is not stirred and the electrode is kept stationary. This type of data can come from another system you may have a film in which diffusion can happen. Then I may or may not be able to use the semi infinite Warburg Impedance there. So, you have to know something about the system. Here, they have modelled this. They have not shown the model fit they have not tabulated the complete model. What they have done is different duration. What is the value of R_t? Is it increasing decreasing and then they have interpreted it saying that poisoning causes. The data is good what happens when you have poisoning is clear from that. Whether this is the best model is arguable. And describing that you need an inductor and a resistor and saying that this describes relaxation is something that you will see many times whenever they are modelling something you have seen an inductor they will say describe some relaxation of adsorbed species.

I am not sure that is the best way to describe. Relaxation of adsorbed species could possibly mean they are interpreting it one form of $d\theta/dE$ but then $d\theta/dE$ can give you a capacitive behaviour, can give you an inductive behaviour. Capacitive meaning whatever spectra you get can come from another system which contains electrical resistance and the capacitor. It does not mean this variation of surface coverage potential acts a capacitor in the sense that it stores charge for you. Just like if you use an inductor it does not mean there is a behaviour like a coil with magnetic field. It just means whatever spectra you get here can be mimicked by another electrical system. I just wanted to show you that this is an example of interpretation of data.

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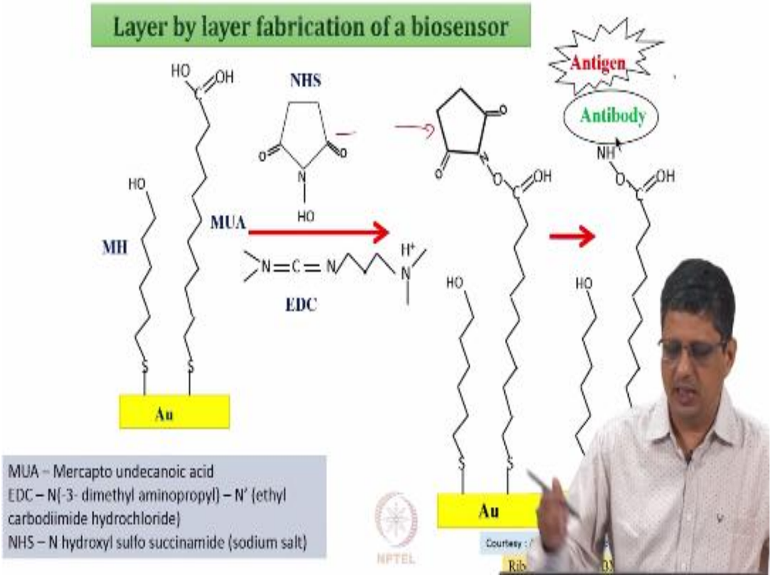

Layer by layer fabrication of a biosensor

MUA – Mercapto undecanoic acid
EDC – N(-3- dimethyl aminopropyl) – N' (ethyl carbodiimide hydrochloride)
NHS – N hydroxyl sulfo succinamide (sodium salt)

Third to give you a little bit of background. In biosensor, you want to detect presence of something called antigen. Antigen could be a parasite [malaria parasite], could be a dengue virus or some chemical that is specific to dengue virus. That virus may release a chemical if you detect that chemical in the blood sample of a person you can see this person is affected by dengue. You can either detect the virus or the chemical that is associated with the virus released by virus but it is marked like if you see this chemical in the blood this person has been exposed to this virus or this bacteria. The bacteria is called antigen. That chemical is also called as antigen. Whatever our body produces in response to that is called antibody. So biosensor here is something here where you want to detect the antigen.

So, what you want to have is an antibody which is specific to this antigen. Now we want to prepare an electrode on top of the electrode you attach somehow suitably couple an antibody, cover the surface with antibody. After that you expose a bloodstream. The bloodstream may or may not contain the antigen if the person is not infected it should show nothing. If a person is infected, that antigen will bind to this antibody now it should show an increase in impedance. At least that is the expectation. So to bind an antibody to an electrode you have to go through certain steps. Gold electrode is normally used although there are many other combinations available now but it is kind of a starting point. Organic chemicals like alcohols, and acid which contain sulphur it is called Mercapto, these chemicals are first used to form what is called self-assembled monolayer (SAM). Sulphur has an affinity to gold so you put these chemicals they will all line up in this fashion or that is again the expectation. So, if we have an area I put these chemicals most of the area will be blocked and these chemicals will line up like this. So, it is called it is assembled on their own we are not doing anything to specifically assemble in a particular fashion, self assembled and it forms a mono layer, one layer. Of course it is not 100% true. It may assemble in different orientation and it may not assembled in some areas. Those are there, but if it works as we expect its going to form a SAM. Then the SAM is not the reason we are doing all this because the anti body is not going to just sit on the surface well. So, we want to make the antibodies sit on the surface means we need to put glue. And it does not work with one glue. We need to do one chemical that is MUA MH, in addition we put two other chemicals. you have to expose a gold to this for a certain number of hours, 12 hours 18 hours 24 hours it forms a mono layer and then we expose to these chemicals for a couple of hours. So, it is not one layer of glue it is a multilayer glue. Antibody can be coupled to this using these chemicals. So, these chemicals form a bond. First these chemicals form a bond then these chemical forms a different structure and then if you put the antibody it is going to sit on top. If I expose the antibody to the gold it is not necessarily going to stick well. Not only that, antibody is a large molecule it will have many orientations. Ideally you want it to be exposed such that when the antigen comes it is able to bind. If that is looking like this when the antigen comes it would not bind.

So, there are difficulties but right now the expectation is antibody will be attached to this with antigen coming and sitting on top of that if the solution has antigen. So you have to build the electrode like this and then keep it ready. When somebody gives a blood sample you will put a drop of it here measure the impedance and if it is high you will say depending on how high it is you will say you are exposed to this virus or this bacteria, and level is serious, moderate, initial level whatever that is. These long chains are the glue, right? S is binding to the gold. We need S here you need long chains here by the way again I am not showing you really per scale it is not that antibodies is going to be small antibody is going to be actually very large but then it is going to go out of the slide so do not think it is drawn to scale it is a just a way to see.

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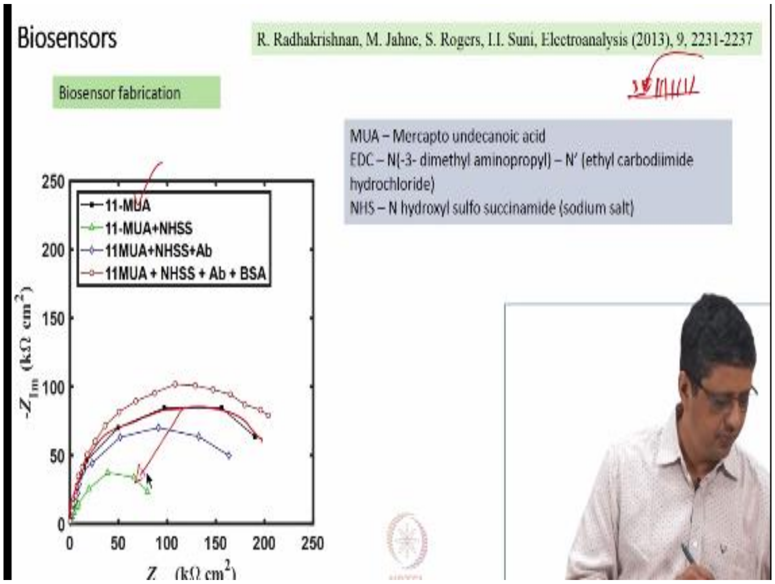

Biosensors

R. Radhakrishnan, M. Jahne, S. Rogers, I.I. Suni, Electroanalysis (2013), 9, 2231-2237

Biosensor fabrication

MUA – Mercapto undecanoic acid
EDC – N(-3- dimethyl aminopropyl) – N′ (ethyl carbodiimide hydrochloride)
NHS – N hydroxyl sulfo succinamide (sodium salt)

This is the idea and after you exposed after you attached the antibody to this electrode, we normally saturate with one more bio-chemical called BSA bovine serum albumin that has a good affinity to gold. So wherever the SAM is not formed if certain area is not exposed to it is exposed to SAM but it is not attaching, BSA will go and block that area so that the antigen does not come here sit here. Antigen or any other chemical in the blood should not come here and sit here and increase the impedance. So before the exposing to blood after putting the antibody we initially feel that SAM should block every area and then the top of which we put EDC NHS and top of which you put the antibody, hopefully the entire surface is filled and antibody is sitting outside and waiting for antigen to come and capture that.

We cannot be sure there might be vacant areas so fill it with BSA. BSA will attach to the gold but not to these antibodies. Again that is the expectation and when you actually see it is not that easy. At least that is what we are seeing in our lab. We have to do it in a very very controlled fashion otherwise it is not easy to get repeatable results. Coming here this is a published data. For bare electrode is not shown. When you put SAM layer impedance in the range of 200 kΩ cm^2 in the real value, imaginary value is around 50 so you can see it is a large value. When you put NHS and it actually decreases.

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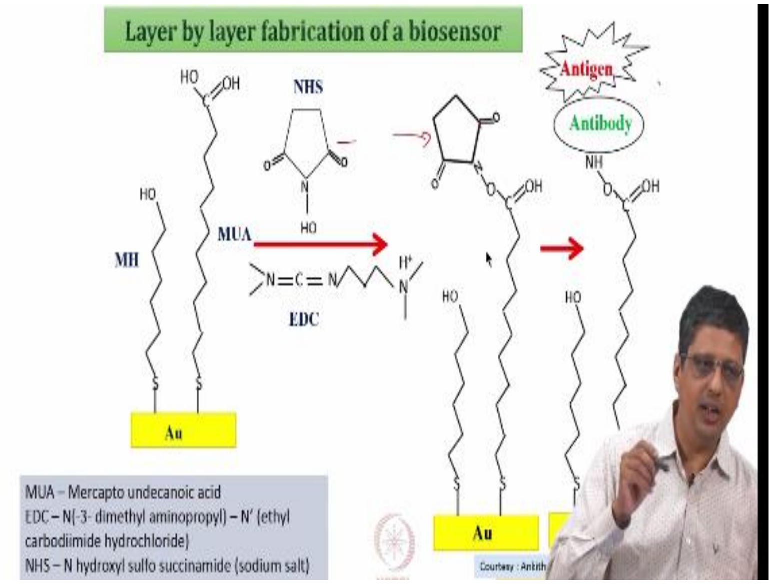

Layer by layer fabrication of a biosensor

MUA – Mercapto undecanoic acid
EDC – N(-3- dimethyl aminopropyl) – N' (ethyl carbodiimide hydrochloride)
NHS – N hydroxyl sulfo succinamide (sodium salt)

Courtesy : Ankith

What that means is, it is not completely blocking. When you put the NHS it allows the reaction to happen. This reaction is usually Fe^{2+} to Fe^{3+}. That means open areas will allow some of the reactions to happen even in the areas with SAM, but they will allow the reaction to happen at much slower rate. When I put SAM and NHS it allows the reaction to happens at a faster rate, at a little faster rate.

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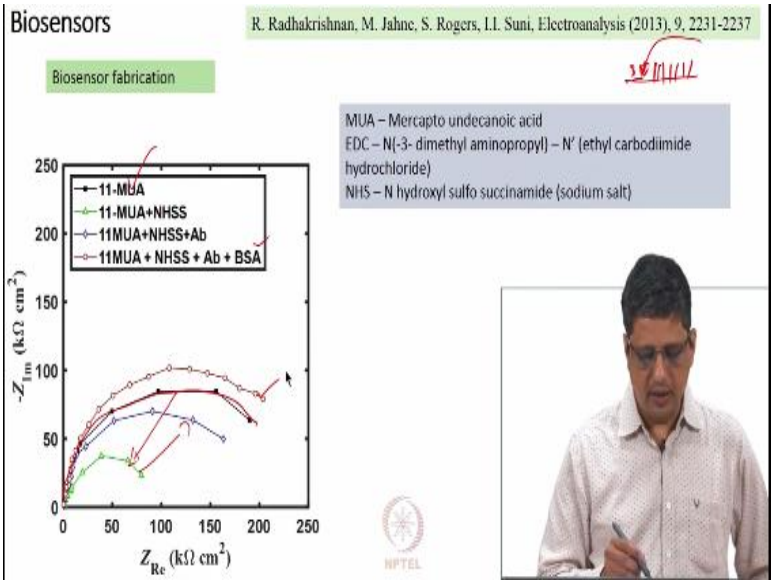

Biosensors

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Biosensor fabrication

MUA – Mercapto undecanoic acid
EDC – N(-3- dimethyl aminopropyl) – N' (ethyl carbodiimide hydrochloride)
NHS – N hydroxyl sulfo succinamide (sodium salt)

That is why the impedance comes down. And then the group has attached the antibody, impedance is increased. When you expose to BSA and you block the remaining area and you can again see it is increasing. That means there were some vacant areas where BSA is blocking. Now this electrode is ready for testing.

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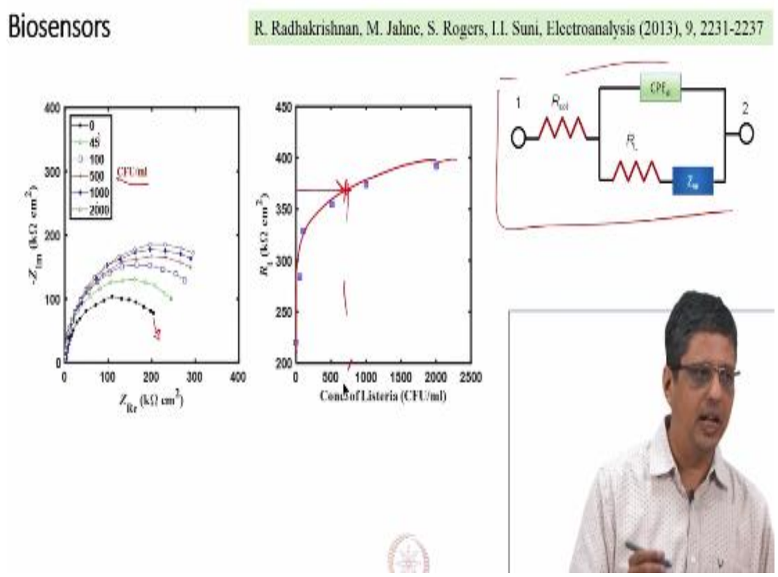

Biosensors

R. Radhakrishnan, M. Jahne, S. Rogers, I.I. Suni, Electroanalysis (2013), 9, 2231-2237

This electrode when you expose it to solution which does not contain the antigen and this is for a particular bacteria I suppose listeria or such bacteria and I do not remember the name now, when you expose to different quantities is expressed in what is called colony forming units per ml. You can think of it as concentration, you have higher concentration here impedance actually increases. And this is the model using the circuit. Typical circuit of solution resistance, double layer represented by CPE, charger transfer resistance and Warburg. And what they show is a plot of charge transfer resistance with respect to colony forming units. Again it forms something like Langmuir Isotherm although it has not really saturated yet. What people ideally want is a linear regime where higher concentration gives you proportionately more signals.

But what they got is a nonlinear one but yet if you take an unknown solution if the charge transfer resistance comes out to be 375 kΩ cm^2. You would say this likely to have listeria of this much concentration. And of course, this is also tested with other type of bacteria and they say that it does not offer any significant increase that means the antibody is specific. It is not binding to any other bacteria. The reason you are doing this is because what if some surface is still exposed and this antigen is coming and binding maybe some other chemical in this solutions is coming and binding. So you normally will test it with other type of material that is likely to be present. That is looking for specificity. Is it specific to this entity this antigen or is going to be blocked by anything?

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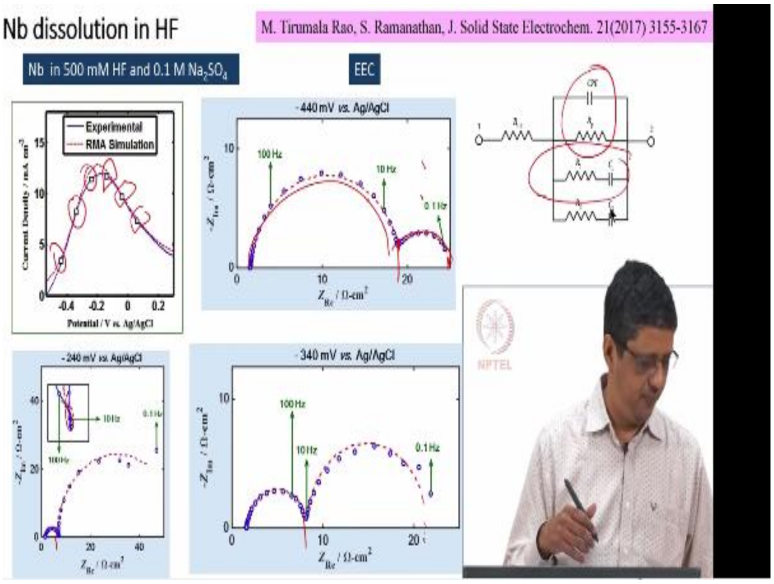

Nb dissolution in HF

M. Tirumala Rao, S. Ramanathan, J. Solid State Electrochem. 21(2017) 3155-3167

Nb in 500 mM HF and 0.1 M Na_2SO_4

EEC

The last one is data from our group. Polarization shows an increase in current and then decrease. It offers passivation. This is niobium which is the metal like tantalum. It does not dissolve in acid except in hydrofluoric acid. When they I say it does not dissolve I mean if we take very concentrated sulphuric acid, it will probably dissolve in PPB level but not to a level where you think of it as a corrosion in a short term or even in medium term it is not going to be a big problem. HF it will etch at a significant rate. If you increase the potential, niobium form niobium oxide. At normal atmosphere it will form a very thin oxide if you go to higher potentially especially if you expose it in solution with sulphuric acid any of this where you can have water or oxygen present it will form a thicker oxide. And what is called passivation even in HF, if you go to the large enough potential, it will form a thick oxide depends on what is the concentration of HF. If you have a small concentration very quickly will form a thick oxide and if I have a large concentration because it dissolves the oxide fast I will have to go to very high potential to get thicker oxide. Now we can get impedance spectrum. We have taken it a 3 different potentials in the region where current increases and then 3 different potential in the region where current decreases.

So, it forms 2 semicircles and this is in rotating electrode. So if you increase the rotation beyond certain limit mass transfer is not a problem. So we say it is all kinetic limited. 2 semicircle but then the semicircle diameter increases this 1 st semi circle diameter decreases. It goes from close to 18 to 9 to even less than that. 2nd semi circle diameter increases right, it ends at around 25 not really increases. It is probably similar here in the sense of being in the larger side and there is a small loop here. So this 1st and 2nd were modeled using 1 and 2. 3rd if I want to model, this 1st and 2nd were modeled using only 1 RC element I will get 1 semicircle from here that is a high frequency loop, I will get 1 semicircle from here that is the low frequency loop. Here again 2 semicircles are sufficient, I mean 2 RC elements are sufficient, 1 Maxwell element is sufficient.

Here to model this inductive loop I have to use either inductor or I have to use RC with a negative value.

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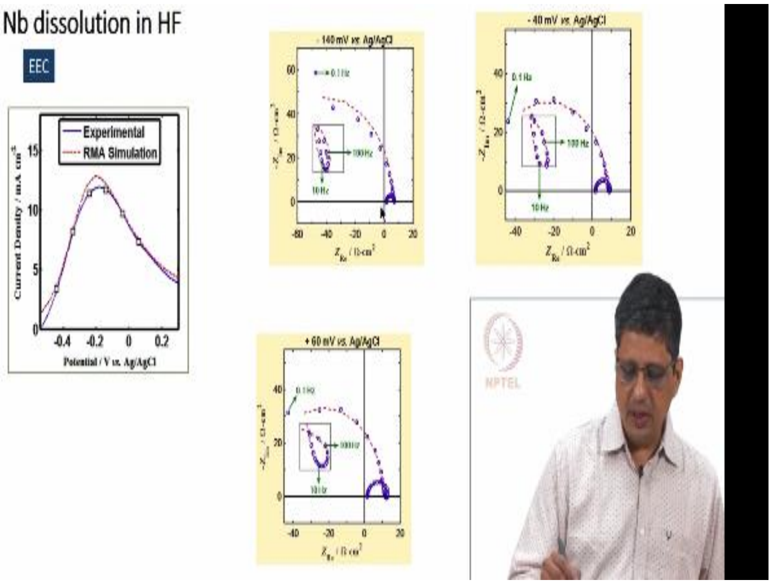

Nb dissolution in HF

EEC

You can get data in the passive region you get something which is with frequency inductive loop which comes clear at higher voltages but it is very small unless you zoom you would not be able to see at the lower potentials. Again you can model this with the same circuit.

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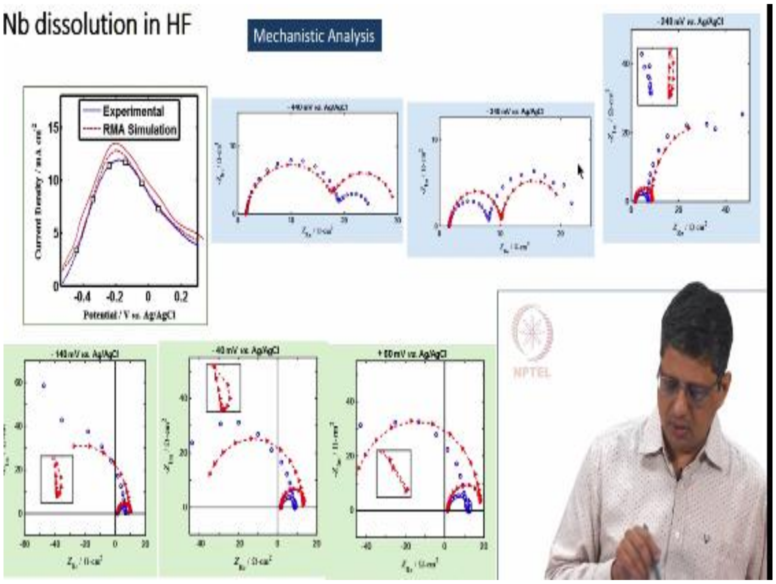

Nb dissolution in HF

Mechanistic Analysis

But then getting physical interpretation is a lot harder. So what we have done is to use mechanistic analysis. Fit is not as good. First of all in EEC, you do not even predict the value of polarization current. That means I am not predicting how the current will vary. I just modeled the impedance spectrum one spectrum at a time. Here we predicted the current, we predicted the impedance spectrum match is we can say qualitative. Meaning, whatever main feature you see we can see here may be semi quantitative to say somewhat similar to this. It is definitely not as good as what you would see in equivalent circuit analysis. However just to show that you can predict the feature although not the data as well.

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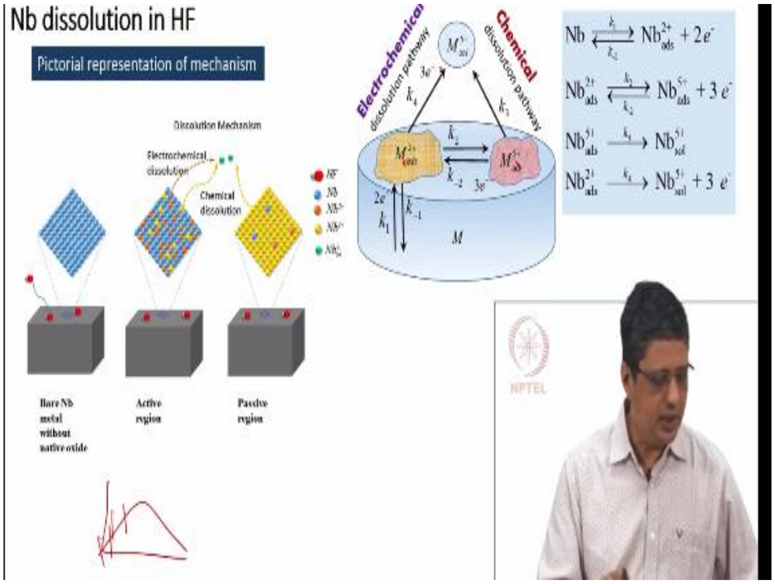

Nb dissolution in HF

Pictorial representation of mechanism

$$Nb \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Nb^{2+}_{ads} + 2e^-$$

$$Nb^{2+}_{ads} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Nb^{5+}_{ads} + 3e^-$$

$$Nb^{5+}_{ads} \xrightarrow{k_3} Nb^{5+}_{sol}$$

$$Nb^{2+}_{ads} \xrightarrow{k_4} Nb^{5+}_{sol} + 3e^-$$

However, what we get out of this is the following. We propose a mechanism like this: niobium gets oxidized to sub-oxide, NbO, which gets oxidized to what is called pentoxide. This is the most stable form but this is also possible. And niobium can get oxidized to sub oxide, both are present on the surface and the pentoxide can dissolve. That is one part way. But that path way will not give me an impedance spectrum like this. It will not give me a current potential diagram like this. So I will have to propose another reaction which says sub-oxide goes into solution while losing 3 electrons. That is Nb^{2+} goes into solution by losing 3 electrons. If I do not have this step, I will definitely not get the curve like this for current potential diagram. I will definitely not be able to get all the features in impedance spectrum.

I may be able to get 1 spectrum in the active region that I can fit well even in this model if I fit only 1 or 2 spectra. I can fit lot better than what I have shown here. But we want to simultaneously fit all the spectrum that means fit may not be as good but this is a better description where 1 model fits all the data at multiple potentials. It also predicts the polarization data correctly. This is better than using a smaller set of data or 1 impedance spectrum. And this gives an idea using this model saying this model seems to describe this phenomenon reasonable well. Let us see what it predicts when they we go to low over potential. This curve mostly bare niobium any sub-oxide and pentoxide that is formed is taken into solution. I know the rate constants because of time and space I am not sure showing you all the rate constants in tabulated form, but you have the values of rate constants you can predict what will be the surface coverage of θ_1, θ_2 as a function of potential.

When you go to mid-potential, what do you see is some niobium oxide is present as pentoxide some is present as sub oxide NbO and some vacant surfaces is also present even though they are simultaneously dissolving. Some of the niobium is getting oxidised to NbO some of the NbO is getting oxidised to Nb_2O_5. Some of it is going into solution some of the oxide is also going into solution but the oxide formation rate is more, sub-oxide to pentoxide is more. Therefore under study state condition surface coverage is more for both of this. When we go to very high potential what happens is pentoxide becomes more or less covers the entire surface.

There is still some niobium left there is still some sub oxide is left, under study state condition. Left meaning I do not mean to say that pentoxide remains there. What I mean to say is net if I look at it now verses if I look at it later, surface coverage, which means some pentoxide might have gone into solution this might have become niobium now. Because underlying metal is exposed some of the sub oxide might have gone into solution and expose this as underlying material. Some of the sub oxide converted to pentoxide. That means it is not moved out but the colour has changed. Colour here is just representation. Some of the niobium would have converted to sub-oxide but net if we look at it now verses a few seconds later on the average I would say maybe 95 % will be pent oxide 3% may be sub oxide, and 2 % maybe niobium. I do not mean to say the locations remains the same I mean to say the surface coverage when I look at it on the average it is going to remain the same under steady state condition. And this gives you you a better idea of what is happening compared to saying these are the elements values here although if it is better in that situation. We will stop here now.