Electrochemical Impedance Spectroscopy
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Lecture - 39
PDM

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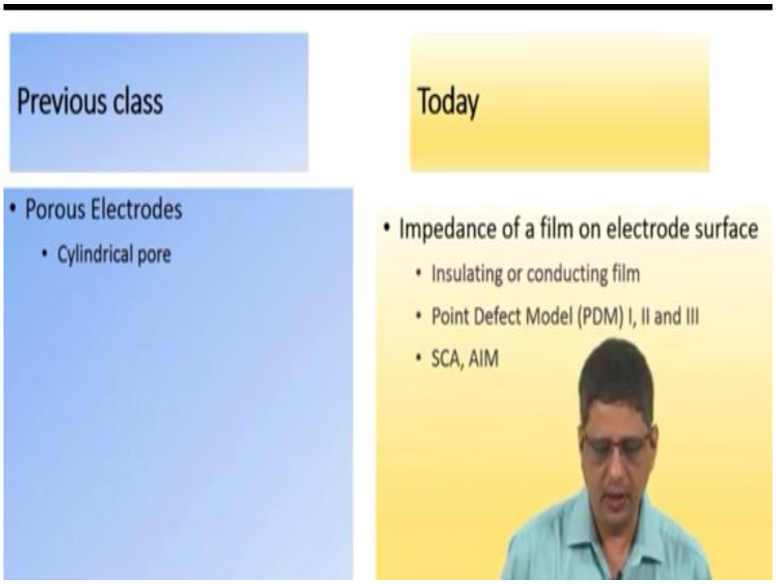

Previous class

- Porous Electrodes
  - Cylindrical pore

Today

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

Yesterday, we were looking at the description of point defect model, (right?) and there are three generations in it. They are classified as I, II, and III.

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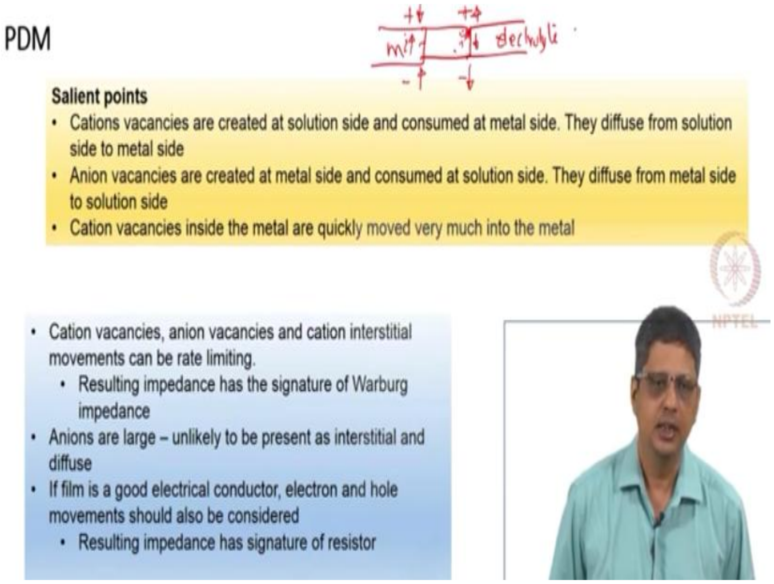

PDM

Salient points

- Cations vacancies are created at solution side and consumed at metal side. They diffuse from solution side to metal side
- Anion vacancies are created at metal side and consumed at solution side. They diffuse from metal side to solution side
- Cation vacancies inside the metal are quickly moved very much into the metal

- Cation vacancies, anion vacancies and cation interstitial movements can be rate limiting.
  - Resulting impedance has the signature of Warburg impedance
- Anions are large – unlikely to be present as interstitial and diffuse
- If film is a good electrical conductor, electron and hole movements should also be considered
  - Resulting impedance has signature of resistor

And after that, we will see other variations of that. So, based on what we have seen, we have a metal *here*, we have a film and we have an electrolyte *here*. They [the authors] looked at a total of 7 reactions, okay? So, on one side, cation vacancies are created. Cation vacancies are denoted by "+" here. Actually, it is vacancy and they are created on solution side and they are consumed on the metal film interface.

Anion vacancies are created on the metal film interface. And they are consumed in the film solution interface.

Interstitials… cation interstitials are formed here, "*i*" is formed here and "*i*" is consumed here and the 7th reaction is dissolution of this, it is a…, it [the dissolution] can be chemical reaction, it can be an electrochemical reaction, depending on whether the cation oxidation state in the film and cation oxidation state in the solution, are different or the same. If they [the oxidation states of cation in film and in solution] are different, then you have an oxidative or electrochemical reaction. If they are the same, it is just a chemical dissolution, ~~but~~ that is just film dissolving into this [solution].

So, these are total 7 reactions. So, any of this can be rate limiting. We have not yet considered the movement of electrons or holes through this, but that also should be considered. If number of electrons that are formed or holes that are formed, …

If we have many electrons, if it [the film] is basically an electronic conductor, that will carry most of the current. [Then the] diffusion of the ions will not carry that much current. Diffusion of the vacancies will not carry that much current. Basically, it [the film] will appear like a resistor.

When it is not a good electronic conductor, only then we have this issue [or need to model using PDM]. Or [if the] number of [available] electrons are very few, or [if the] number of [available] holes are very few, okay, then we have these vacancies going through this [film] or interstitial going through this [film] for conduction, okay?

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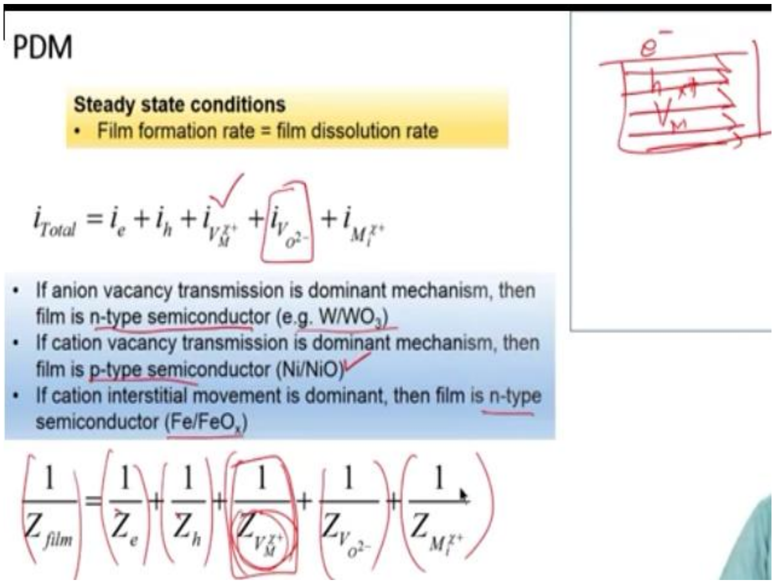

PDM

Steady state conditions

- Film formation rate = film dissolution rate

$$i_{Total} = i_e + i_h + i_{V_M^{\chi+}} + i_{V_{O^{2-}}} + i_{M_i^{\chi+}}$$

- If anion vacancy transmission is dominant mechanism, then film is n-type semiconductor (e.g. W/WO$_3$)
- If cation vacancy transmission is dominant mechanism, then film is p-type semiconductor (Ni/NiO)
- If cation interstitial movement is dominant, then film is n-type semiconductor (Fe/FeO$_x$)

$$\left(\frac{1}{Z_{film}}\right) = \left(\frac{1}{Z_e}\right) + \left(\frac{1}{Z_h}\right) + \left(\frac{1}{Z_{V_M^{\chi+}}}\right) + \left(\frac{1}{Z_{V_{O^{2-}}}}\right) + \left(\frac{1}{Z_{M_i^{\chi+}}}\right)$$

If I look at the current through *this*, through the film, I will have current because of electrons, I will have [current] possibly because of holes. We will have current because of the movement of, metal vacancy or cation vacancy, we will have current because of movement of anion vacancy, and we will have current because of movement of interstitials.

In case the anion vacancy is the most dominant mechanism [of transport], the film will appear as a N-type semiconductor, okay. An example is tungsten with tungsten oxide formed on the surface; so obviously, it means that electronic conduction, hole conduction ~~they~~ are all much, much smaller compared to this [current transported through anion vacancy movement], okay. Cation vacancy conduction is [also] not that high. Cation interstitial conduction is [also] not that high. The major current carrier is the anion vacancy [in this example].

In case (the cation vacancy is dominant or) transport of cation vacancy is dominant [mechanism], right, the film will be [have] as P type semiconductor. An example is nickel oxide; and if cation interstitials movement is dominant, then again it [the film] will appear as an N type [semiconductor], okay? So, depending on which [species] movement is dominant, it [film] is going to appear as [an] N type or [a] P type semiconductor.

If hole [movement] is dominant, [then also the film] ~~it~~ is going to appear as a P type, but the conductivity of that film is going to be very high. If the P type behavior arises from the cation vacancy transmission, then that conductivity will be poor~~er~~. If ~~it~~ [the P type behavior] is because of holes,… (the holes will move fast, their mobility is high compared to the vacancy movement. So) that will also appear as a P type semiconductor, but then it will have much better conductivity. In general, current can be carried by any five of these, or all five of these pathways. Since they are occurring in parallel, we will have to add the admittance to get the net admittance.

So, we will write the film admittance is going to be the admittance due to the flow of electrons, [admittance due to] flow of holes, [admittance due to transport of] cation vacancy, [admittance due to transport of] anion vacancy, and [admittance due to transport of] cation interstitial. Typically, one of them [i.e. one of the *impedance* values] will be a low value. If the current is high, the impedance is going to be low, [and] admittance is going to be high. If I say "This cation vacancy [movement] is the dominant [transport] mechanism", *this* will be a large number, *this* will be a small number, *this* is going to be a large number, and we can neglect the remaining [terms]. If they are comparable, then you have to use all of them together.

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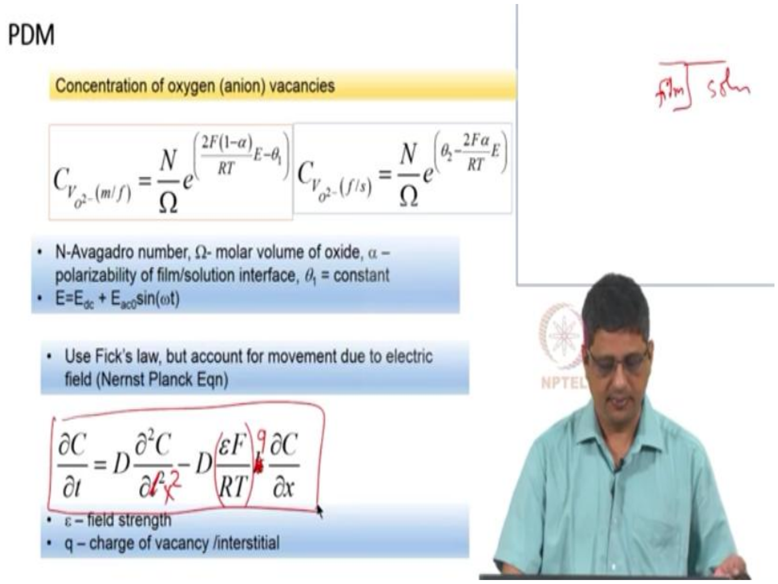

PDM

Concentration of oxygen (anion) vacancies

$$C_{V_{O^{2-}}(m/f)} = \frac{N}{\Omega} e^{\left(\frac{2F(1-\alpha)}{RT}E - \theta_1\right)} \qquad C_{V_{O^{2-}}(f/s)} = \frac{N}{\Omega} e^{\left(\theta_2 - \frac{2F\alpha}{RT}E\right)}$$

- N-Avagadro number, Ω- molar volume of oxide, α – polarizability of film/solution interface, θ_1 = constant
- $E = E_{dc} + E_{ac0}\sin(\omega t)$

- Use Fick's law, but account for movement due to electric field (Nernst Planck Eqn)

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - D\left(\frac{\varepsilon F}{RT}\right) q \frac{\partial C}{\partial x}$$

- ε – field strength
- q – charge of vacancy /interstitial

I am still giving you only a qualitative view of this [point defect model]. I am not showing the derivation [of impedance equations]. And I will also just introduce how these equations are developed, but I am not going to go through the full development [i.e. derivations]. The rate at which the oxygen or the anion vacancies are generated…. (Not the rate which they are generated), The concentration of anion vacancies at the metal film interface, concentration of anion vacancies at the film solution interface, these are given by these equations. Here, N is Avagadro number, this Ω here, it is not the ohm [the units of impedance]… it is not the unit of resistance inside [the film], [Here Ω denotes the] ~~it is~~ molar volume of oxide. α here is the polarizability of the film- solution interface. θ_1 is a constant, likewise θ_2 is a constant, and potential here is given by E, which is [the algebraic sum of] DC and AC.

Basically, there are expressions to calculate the concentration of anion vacancies, concentration of cation vacancies, diffusivity, (estimation of diffusivity, you can put a diffusivity term there).. And then, you can calculate based on fitting it to the experimental data, but it is possible to develop the equations while accounting for the presence of electric field and accounting for the fact that these are charged entities.

So, essentially we are using the equation, which is similar to Fick's law (and this has to be corrected)… but this accounts for the fact that these entities are charged. ε is the field strength, (I think I missed the *q* here). "*q*" is the charge of vacancy or interstitial, F (of course) is Faraday constant, R_t… We know all these values, [and the] temperature and then [the] universal gas constant. So Nernst Planck equation is used when we have (movement) diffusion, [and] if the entities are charged. We have diffusion because of concentration gradient. We [also] have diffusion or movement because of electric field, and these two together, accounting for both the concentration gradient and the electric field, (of course in one dimension)... [we can estimate the net movement].

Qn: Sir, there is no influence of mass on this equation?
Ans: Diffusivity [will play a role]… Why would the mass come [in this equation]?
Qn: Diffusivity is characteristic [of the entity], right?
Ans: Yeah, but why would mass come there?
Qn: As in, if ~~it~~ [mass] is more, it will diffuse slower.
Ans: See…You are saying if it is larger volume, it may go slowly. That means diffusivity will be [a] small number. They are basically using the term diffusivity here, *D* here to account for [all the factors]. This *D* is [the diffusivity of a particular species] in this crystal or this amorphous film, (in this medium). Diffusivity [of this particular species] in water is going to be different for

[that of] the same species [in this film]. [In water] it is going to be [an] ion, of course surrounded by hydration sheet. So, diffusivity here obviously it means diffusivity in this medium.

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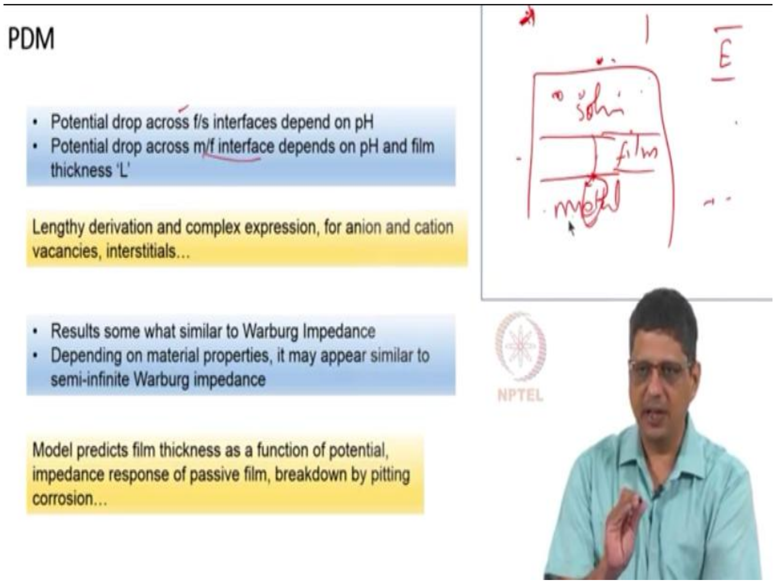

PDM

- Potential drop across f/s interfaces depend on pH
- Potential drop across m/f interface depends on pH and film thickness 'L'

Lengthy derivation and complex expression, for anion and cation vacancies, interstitials…

- Results some what similar to Warburg Impedance
- Depending on material properties, it may appear similar to semi-infinite Warburg impedance

Model predicts film thickness as a function of potential, impedance response of passive film, breakdown by pitting corrosion…

So you can understand why this is called *point defect model*, right? We have a lattice in which vacancies are present, and these vacancies are of course called *defects*, and because it is present in the lattice, these are called *point defects* and since that is used to explain the conductivity and the impedance, this is called point defect model, okay.

Potential drop across this interface… So when you apply a potential normally in a metal solution interface, we would say "Potential drop occurs very close to the double layer". (Not very close to that), Potential drop occurs *across* the double layer; And if solution resistance is negligible, it is going to be, more or less constant potential in the solution. And in the reference electrode, again there is going to be a potential drop, but whenever we vary the potential, using the potentiostat, that change [in potential] occurs only *here* [at the working electrode], because the reference electrode potential drop is ~~a~~ fixed.

If solution resistance is significant, then (depending on the current value), you may have ~~a~~ potential drop in the solution also. Now when you have a film, the double layer occurs *here*. There is a potential drop. In addition, there is a potential drop across *this* film and in addition, there is a possible potential drop across the metal-film interface. So, what we apply is from *this* location to other location in the reference electrode, and *there* [at the reference electrode] we assume [that the potential drop] ~~it~~ is fixed anyway.

In these calculations, we are going to assume [that the] solution resistance is not that high. The resistance due to the film is going to be usually much, much larger [than the solution resistance]. When we look at the potential drop across the electrode and if it is measured with respect to particular reference electrode, we have to consider three potential drops. 1. Potential drop across the film-solution interface, [which] depends on the pH. It is going to be linearly related to the pH.

And of course, [it is also going to depend on] the applied potential… If you apply certain potential, part of it will occur *here*, part of it will occur *here*, part of it will occur *here* and part of it will occur *here*. How much occurs *here* depends on the pH and the applied potential. How much occurs *here* basically depends on the thickness of the film and of course what we apply [i.e. applied potential].

How much occurs *here* is going to be (E metal-film… is going to be) basically (E applied - E film - E film solution). Normally, in the previous example where we just had a metal, whatever we apply… if I say solution resistance is negligible, we are going to say *this* is just occurring across *this*, with respect to *this* reference electrode. Whatever we apply is applied across the interface. That is how we have done the calculations [so far]. Now, we are going to say "Whatever we applied is split into three [parts]. One is going to depend on pH, [and] another is going to depend on the film thickness. So, this potential drop across the metal film interface is going to depend on both pH and the film thickness, and naturally dependent on how much we are applying, how much potential we are applying.

Now, when you solve these equations, you get a result, which is somewhat similar to Warburg impedance. It might look similar to semi-infinite Warburg impedance, it might look similar to bounded Warburg impedance; you know you can visualize that the diffusivity is going to be much, much smaller than the diffusivity of a species in solution, right? Another way of looking at this to say that the film thickness is going to be very high, when you compare it to the diffusivity.

You cannot compare it [the film thickness] directly with the diffusivity. The units are different. But you can visualize [that] if the diffusivity is small or film [thickness] is large, they will have similar effect. So, [many] times, it will appear similar to a semi-infinite Warburg impedance. This model is able to predict successfully [the impedance spectra of] ~~for~~ different types of metal solution interface or film solution interface.

How [does] the film thickness vary with the potential? If I have higher potential, you will normally expect a thicker oxide, but it [film thickness] is not going to necessarily vary linearly [with potential]. [This is] because dissolution rate, formation rate, formation by different mechanisms, all these things have to be considered [while estimating film thickness]. *This* (PDM) is able to predict (for many cases), the [film] thickness variation with respect to potential, [and also the] impedance response for different films; and there is a phenomena called pitting corrosion [which is also explained by PDM].

If you have a solution, a metal here with a film on top, right? Uniform corrosion is everywhere [metal] dissolving at some way. Pitting corrosion usually refers to the case where, if you look at the surface, there are clear pits. That means it [the corrosion] is localized. It occurs [only] in some locations. Of course, it is dangerous, because it is attacking the material and it typically goes below and keeps corroding more. So, on the surface you will see [a] few points, [you will see] some corrosion, but actually corrosion is…, it can occur deeper.

If you see full corrosion everywhere, it is not such a problem; ~~meaning~~ I mean that it *is* a problem, but you are [usually] prepared for that. If you see rust everywhere, you know it is getting weaker. If [there are only a] few pits, you think “Everything is okay”, unless you look very carefully; it looks like “Surface is okay”, but actually the material is getting weaker.

And pitting corrosion is seen usually when we have chloride ions present [in the solution]. It happens when you have chloride ions present. It takes some time for the pitting corrosion to occur; meaning, (i.e.) there is an initial period where nothing is happening. “Nothing is happening” meaning, where you do not see any pits. I do not mean to say “Nothing happens”. I mean “Nothing is seen”. There is an incubation period, where nothing is visible and after that, pitting corrosion occurs.

These are experimental observation and this model is able to explain why that can happen. (Let us see if I have prepared a slide for that, if not I will describe it here, okay, maybe not.)

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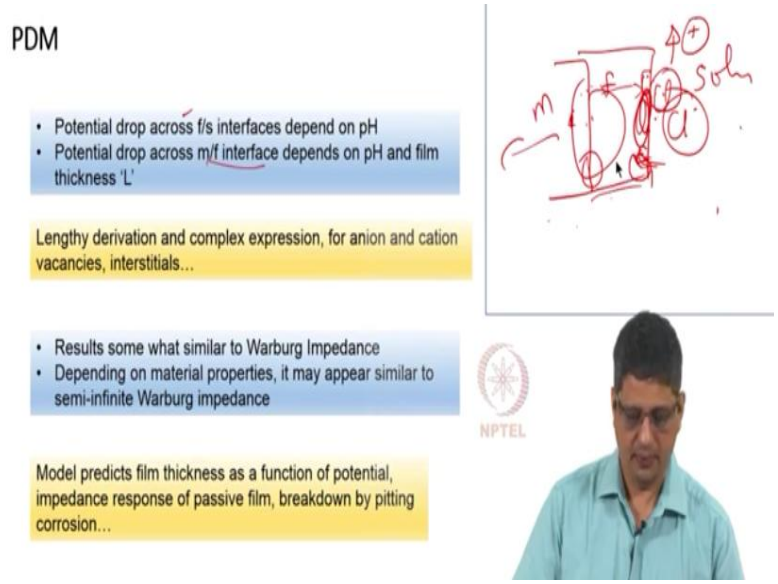

PDM

- Potential drop across f/s interfaces depend on pH
- Potential drop across m/f interface depends on pH and film thickness ‘L’

Lengthy derivation and complex expression, for anion and cation vacancies, interstitials…

- Results some what similar to Warburg Impedance
- Depending on material properties, it may appear similar to semi-infinite Warburg impedance

Model predicts film thickness as a function of potential, impedance response of passive film, breakdown by pitting corrosion…

So, I will just describe qualitatively, what this (model) says. So, in this model, pitting corrosion happens when chloride ions come *here*. Metal vacancies that are generated *here*, right?... The rate of formation of metal vacancies increases. Cation vacancies… (I should not say metal vacancies; I mean cation vacancies). Because of that, cation vacancies move here. That is to say “metal forms metal ion and moves this way”.

The cation vacancies accumulate *here*. Normally, if you do not have chloride…Of course even then, cation vacancies will form *here* and cation vacancies will come *here* and they will be taken up by the metal and they will diffuse inside [the metal] and go [be consumed], okay? If you have lot of cation vacancies *here* [at the metal-film interface] and the rate of consumption of cation vacancy by metal is not keeping up with the rate of arrival of the cation vacancies, you will have void formation.

So, the corrosion does not occur *here…* meaning, it is not becoming a void *here* [at the film solution interface], it is actually becoming a void at the [metal-film interface]. And that happens only in some locations, meaning, where chloride ion accelerates the formation of cation vacancies. It is not occurring throughout *this* [surface]. It may accelerate in some specific locations, where, again, the boundaries meet or [in] certain cases where it is easier for ~~it~~ [the chloride ions] to accelerate [generation of cation vacancies].

In other places, it may accelerate to some level, but not to a large level. Only in certain locations, because of some weakness there, (weakness there, meaning "it may be grain boundary" or "it may have some other defect already present"), it accelerates. And cation vacancies, which are formed *here,* will move by diffusion and it creates a void at the metal-film interface and then the void grows. So, the void actually grows from *inside the film*.

It is not that "dissolution occurs *here* more rapidly on the film surface, on the film solutions interface". That also explains why it takes some time… because the vacancies have to accumulate to some level [some extent]. So, it explains why that incubation time is seen experimentally.

Some theories were [proposed earlier to explain pitting], which said [that] chloride ion is diffusing in and coming *here* [to the metal-film interface] and attacking it, but it is not likely for a large anion to move through a film. It can come in and get incorporated [in the film] and then it can go [further inside] by [vacancy] jump. That is possible, but one chloride ion coming *here…* [or a] few chloride ions coming *here* will not cause such a void, whereas chloride ion sitting *here* [on the film solution interface], but accelerating this (formation of cation vacancy) will definitely cause *this* [pitting] issue.

Typically pitting is seen when you have chloride or fluoride [ions]. Fluoride is not common in environment. Chloride is common in the marine environment.

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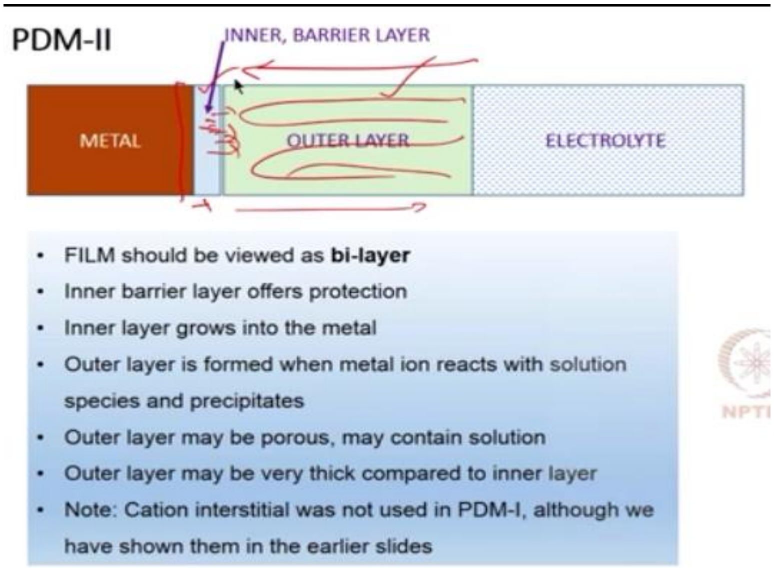

PDM-II

- FILM should be viewed as **bi-layer**
- Inner barrier layer offers protection
- Inner layer grows into the metal
- Outer layer is formed when metal ion reacts with solution species and precipitates
- Outer layer may be porous, may contain solution
- Outer layer may be very thick compared to inner layer
- Note: Cation interstitial was not used in PDM-I, although we have shown them in the earlier slides

So, [in] the first level of model [i.e. PDM I] actually cation interstitials were not used, although [here] I described it with 7 equations. They had [only] 5 equations [in the first generation PDM I]. There were no (cation vacancy or) cation interstitial formation, and consumption, but, for completion sake, I wanted to introduce [you to the complete] model.

Second level [second generation PDM] is to recognize [that] the film that is seen is actually not uniform all the time. Most of the time, it contains two layers, one is a thin layer, but it offers protection, it is called *barrier layer*. Second is an outer layer, it can be porous and that is formed when this cation interstitial as well as the dissolution of the film releases cations *here*. They can interact with the solution species and form a precipitate. This can be very thick compared to this film [barrier layer]. *This* [barrier layer] can be few nanometers. *This* [outer layer] can be in microns. So, I have kind of drawn it like this.

By the way, everywhere I am not drawing really [to] scale. When I show a metal, and then a film, it is a just a pictorial representation. It does not mean you have a thick film there, even in the previous examples. So, in this case, inner barrier offers protection and *this* layer grows into the metal; and when the cations are ejected out, they react with the solution species, which means this is likely to be porous, outer layer may be porous. It may contain solution and may be very thick compared to this inner layer …

…Which also means when you analyze it latter…if you take this, put it under vacuum… one technique that is used to measure the concentration on the surface or identify the species, this is called XPS... You can find out the concentration of various species on the top, including the oxidation state, by using this [technique]. And depending on what angle you are using for measurement, you can get few nanometers, or even one nm thickness layer can be probed. And then what people do is “Remove the layer, nm by nm”, by a technique called sputtering, okay? (So,) Which means you can monitor the film composition as you go down. *Here* it means, as you go down from the outside to the inside, [we can find how the composition varies]? But if this film is one nanometer thick and if your measurement is [probing a depth of], let us say 5 nanometer or 10 nanometer thickness, you might quickly miss this. It may just sputter through this and quickly pass through this. [Therefore, you may not clearly detect the barrier layer]

So, it may not be that easy to detect it [the barrier layer] using other techniques [such as XPS]. Barrier layer can be very thin. It can offer protection. But if you have a thick outer layer, you may not be able to see it [the barrier layer] that easily by other techniques, okay. You may find the film to be porous. If you are using other technique, you might say “I think the film is porous”; but [actually the film] it may offer a good protection, not because that [outer layer porous] film is offering protection, [but] because the very thin film, just on the [metal] surface [which we are not able to detect using other technique], is [actually] offering protection, okay.

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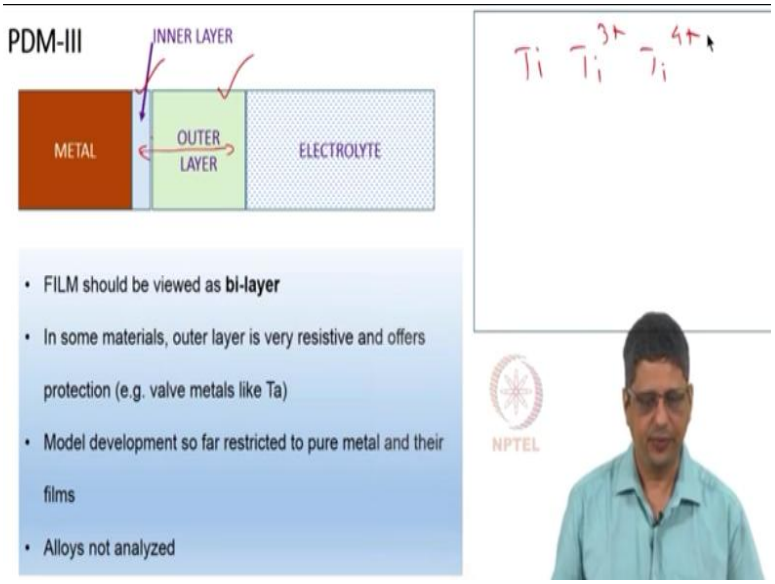

PDM-III

- FILM should be viewed as **bi-layer**
- In some materials, outer layer is very resistive and offers protection (e.g. valve metals like Ta)
- Model development so far restricted to pure metal and their films
- Alloys not analyzed

Ti Ti_i^{3+} Ti_i^{4+}

Then, a third generation [PDM III model was proposed] is to recognize [that] sometimes the barrier layer can actually offer protection, (not barrier layer, I mean the *outer layer*) can offer protection. If it [the outer layer] is very resistive… like materials like tungsten, titanium, zirconium, they have a thin film, which offers protection. And even there, if you ~~consider~~ [assume that] the quality of the film changes with distance [from metal surface], you can say “One is an inner film, one is an outer film. The outer film itself is ~~very~~ [so] resistive that it is protecting this material”, okay?

By the way, everywhere in this model or even [in] what others have presented, we assume that the metal is a, it is a single metal, it is not an alloy. The material is a single metal. If you have [an] alloy, the composition will vary. Even here, the same metal the composition can vary across *this* [the surface], you may have less defects [ion one place, and] more defects at different locations, that is one [type of variation]. [Another type of variation that] ~~What~~ I have not described is “A metal like titanium can be present in Ti^{3+}, Ti^{4+}, multiples oxidation states,…”. [Handling that case] becomes more complex, therefore, we are restricting ourselves to a simpler form of “Ti becoming Ti^{4+}”, [or] “Tantalum becoming tantalum pentoxide”… that is it (Although it can actually exist in other oxidation states also).

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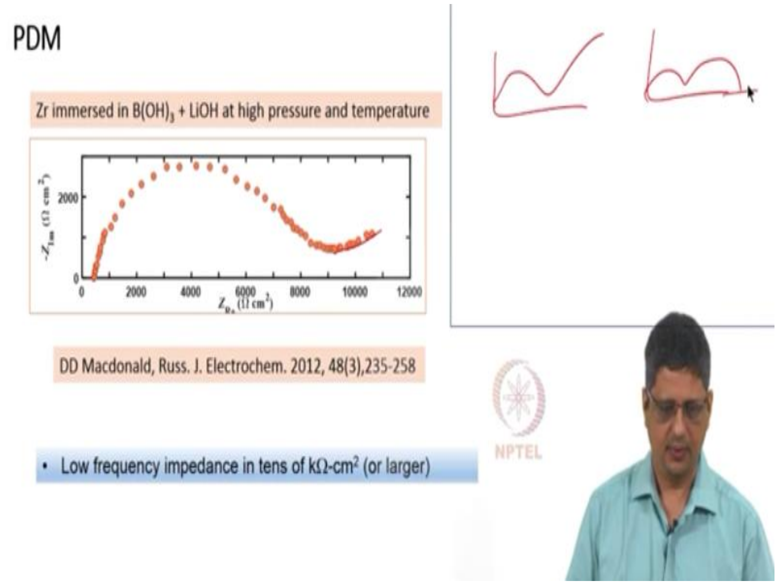

PDM

Zr immersed in $B(OH)_3$ + LiOH at high pressure and temperature

DD Macdonald, Russ. J. Electrochem. 2012, 48(3),235-258

- Low frequency impedance in tens of kΩ-cm^2 (or larger)

And, an example. If you have zirconium immersed in lithium hydroxide and boron hydroxide… This is used ~~for~~ (I think nuclear,) in some nuclear facility, (I am not very sure, okay. Yeah, I think it is used in nuclear facility, okay), high temperature, high pressure for certain types of nuclear reactors. If you look at the impedance, *this* is how it appears. The main feature that I want you to see is it appears with a "Warburg like signature" at the low frequency.

It has [the impedance magnitude is] tens of kΩ cm^2, right? Impedance at the low frequency. Sometimes MΩ, in that range. But the characteristic signature is either this or the film thickness is very small and diffusivity is moderate, you can have something like a "similar to a finite Warburg impedance". Not exactly described by the finite Warburg impedance, but somewhat similar to that.

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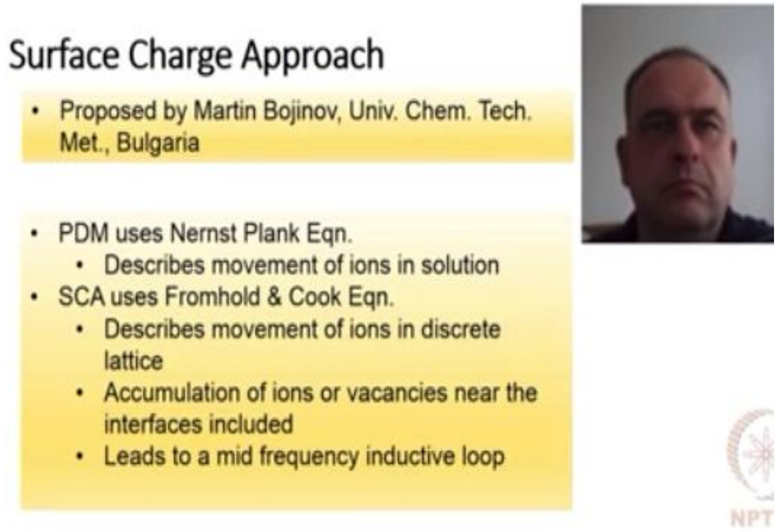

Surface Charge Approach

- Proposed by Martin Bojinov, Univ. Chem. Tech. Met., Bulgaria

- PDM uses Nernst Plank Eqn.
  - Describes movement of ions in solution
- SCA uses Fromhold & Cook Eqn.
  - Describes movement of ions in discrete lattice
  - Accumulation of ions or vacancies near the interfaces included
  - Leads to a mid frequency inductive loop

There is a variation to *this* that is proposed by Martin Bojinov. (I could not get a better picture, so whatever I got, I put here). In the point defect model, what is used is “Nernst Planck equation”, ~~which uses,~~ which assumes, that the medium is continuous; meaning it is used for solution. If a charge species moves in solution, we use Nernst Planck equation to describe the movement, whereas, if you have discrete locations, (which is what is realistic in a crystal), okay?... The equations that are used to describe the movement of charge species in discrete location is little different, okay. It is called Fromhold & Cook equation. That is used instead of Nernst Planck equation. It gives you a slightly different expression. The other thing is, the accumulation of ions in this, right?, You can have cation vacancies on one location, anion vacancies accumulating in another location…Accumulating meaning, the species concentration is not uniform. If it is uniform, you will not have diffusion. It is formed in one location and consumed in the other side. For cation vacancies, it is formed *here*, consumed *here*. Anion vacancies are formed *here*, consumed *here*. So we assume the concentration gradient is going to look like *this*, correct?

It may or may not be linear, we probably assume it is linear, but you can say concentration of anion vacancy is going to be higher *here* and lower *here*. Cation vacancy is going to be higher *here* and lower *here*. If cation vacancy is higher *here* and anion vacancies are higher *here*, naturally the film is not going to be neutral everywhere. We are going to assume it is charged differently at different locations.

And when you apply sinusoidal potential, these charges will also move (or will tend to move). That is one. Second if you really think about it, if *this* is the potential, *this* is the film thickness, okay… Under anodic potential, when you give higher potential, oxidation is more likely to occur. So, metal will form a metal oxide. So if you go to larger potential, you will expect a thicker oxide in the passivation region.

So, if I apply sinusoidal potential, I am increasing, coming back to *this*, decreasing and coming back to *this*. So I can also expect the film thickness will increase, coming back to *this* original [thickness], decrease and come back to the original [thickness]… provided it happens at a very slow rate, the potential variation happens at a very slow rate.

So if I go to low frequency, it is possible that the film thickness varies with potential. Normally, when we apply sinusoidal potential, we say *this* is a DC potential, *this* is the film thickness. I cause a perturbation. I apply an AC. I am assuming the rate of movement of the electrons, holes, vacancies, will vary. I normally do not assume that the film thickness will vary…, but here you can take the variation of the film thickness into account.

We normally think it [variation of film thickness] is very small, but here this model says that may not be small, okay. The presence of the charge…, the distribution of charge at various locations, (right, it is not uniform…) it is non-uniform, that along with this variation of thickness of this film, okay?,,,those are all included in this model and this model predicts that at mid frequencies, you will get an inductive loop.

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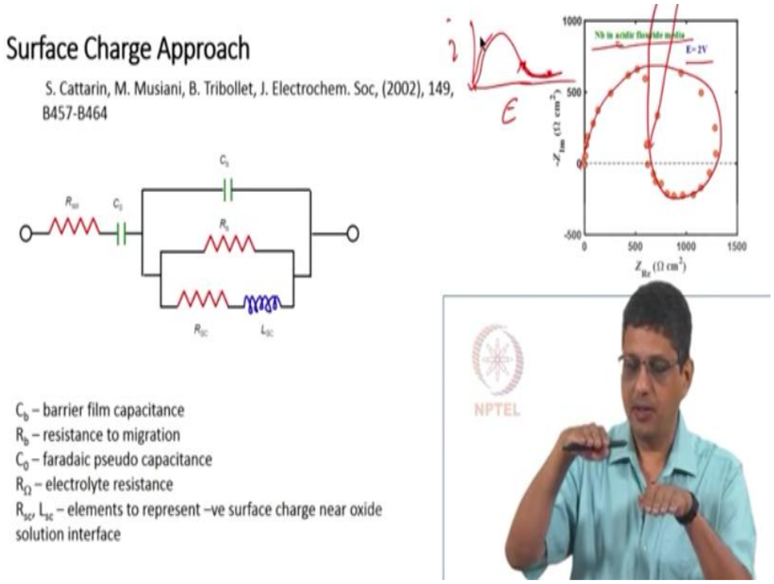

Surface Charge Approach

S. Cattarin, M. Musiani, B. Tribollet, J. Electrochem. Soc, (2002), 149, B457-B464

C_b – barrier film capacitance
R_b – resistance to migration
C_0 – faradaic pseudo capacitance
R_Ω – electrolyte resistance
R_{sc}, L_{sc} – elements to represent –ve surface charge near oxide solution interface

In some cases, that [inductive loop] is seen. The point defect model, without these variations or changes, does not predict a mid-frequency inductance. But when experimentally you see *this* [the mid-frequency inductive loop], …So this is an example, niobium is like tantalum, okay. In acidic fluoride medium, it gives a spectrum, which goes like *this*, not really vertically, it is little bit to the right side and 2 volts, I think with respect to open circuit potential (or I do not remember what it is with respect to), but this is definitely in the region where it is passivated.

Potential and current…Passivated and say that *here* or the region where it is more or less flat current *here*... You see an inductive loop and you see a vertical line going up, okay.

Qn: What do you mean by the passivating region, where is this?

Ans: Okay, when you put niobium in acidic fluoride medium, any HF based liquid, (it can be with buffer, without buffer,) it will dissolve. When you do not apply any potential, it will dissolve at a slow rate. Depending on the concentration… (I should not say slow rate, depending on the concentration, it will dissolve at higher rate or lower rate).

If I give positive potential, the dissolution rate will increase up to some level. The current will increase up to some level, okay. Oxide formation rate will increase. Let us say that the net rate of dissolution in this particular solution is at this level. (I am just going to draw in the air, okay). Metal converts to oxide, oxide is dissolving in into the liquid, okay.

rate of formation of metal oxide, metal converting to metal oxide may be low. If I apply more and more positive potential, I am increasing the rate at which metal oxide is formed. And when it is formed, it is also removed. When I apply large potential, the rate of formation of metal oxide is more than the rate of dissolution. Then, an oxide will form. Now the [film-solution] interface will have a lower potential. I apply this much potential, but certain amount of potential is dropped in the film. Because there is a film present here, significant amount of film present here. Now the remaining potential is going to form *this*. Now the dissolution rate will decrease. Because the rate of formation of metal now is not that much. The rate of formation of metal oxide is not that much, okay. So what happens is "when you give more and more potential, the dissolution rate increases up to some level and then decreases further".

Then it remains more or less flat. It actually increases slightly… and after that, it will again increase when you apply so much potential that the cations will really pass through the film and come out. It does not need the metal to form oxide and then only the oxide dissolution is important… If cation comes out *here* and goes out, that also causes dissolution.

So, this is called *transpassive dissolution*. Beyond passivation, you can have further dissolution, if you go to *that* potential. Now we have seen earlier that the slope of this curve gives us the low frequency impedance, correct? Meaning, if this slope is positive, I expect the low frequency impedance to come and end here. It may come and end like *this*. It may come and end like *this*, it may do whatever and then come, but it is seen somewhere there. If the slope is negative, it will end at *this* location, [on the] negative side.

And of course, I can get [this value] quantitatively also, I look at the slope that gives me di/dE. I calculate dE/di and within experimental data, it has to settle *there*. Here it says *infinity*. [The] Slope is zero [and the] inverse of [the] slope is infinity. Here, slope is more or less zero, inverse of slope has to be very large number or infinity, but we normally expect that to settle at the real axis.

We say if I apply a very slow, sinusoidal potential, current has to follow this. That will happen when *this* behaves like a resistor. If you have a capacitor, regardless of how low this frequency is, the phase will always be 90 °. If you have a resistor (or combination, which reduces to a resistor), then it will settle at the real axis, the phase will be 0 or within noise level, it will be 0 °. *This* curve does not tell us that *this* system will give you a capacitor like behavior.

That means, the potential current diagram does not tell us that low frequency impedance will show us a vertical line. [Consider] Warburg impedance, for example. If I have a semi-infinite diffusion, current will be close to zero, the slope will be close to zero… (Current will not be *close* to 0, At OCP current will be [exactly] zero), slope also will be close to zero.

Warburg impedance goes like this. As far as you can say "It is going to be 45 ° line", as you go to lower frequencies, the magnitude becomes higher and higher, it tends towards infinity as ω tends to 0, phase does not tend to 0, as you can see from this line. Likewise, here, the phase actually goes towards 90 °, so that is modeled using *this* circuit. Solution resistance is there.

"b" here corresponds to barrier film capacitance, this R_b is the film resistance. So we assume there is a solution resistance. There is a film. The film offers a capacitance as well as … It is not a conductor, so it is a semiconductor. It has the capacitance, it has the resistance, resistance to migration of vacancies and interstitials. This C_0 is called Faradaic pseudo capacitance, okay. This can be visualized as the variation of film thickness with potential. That is dL/dE. This surface charge is given by the subscript $_{SC}$.

This model predicts that you will have two elements, resistance and inductance to represent that negative surface charge near the oxide solution interface.. meaning near this place, you have more cation vacancies, lot of anions are present... so you have more negative charge. Of course, you have more positive charge here. If you assume the anion vacancies are produced here, cation vacancies are consumed, so mostly it is filled with cations and they are getting taken up. The vacancies are taken up.

If I understand correctly, the journal article says that this represents the negatives of charge, near the oxide solution interface. This circuit is used to model… Of course, these elements are related to the diffusion and kinetic parameter values. And if I use the circuit, it will predict, "If I go to low frequency, what happens is at low frequency, no current will go through this. This offers zero resistance. This offers some finite resistance together. But this offers the maximum resistance to low frequency”.

So it is going to behave like a capacitor with resistance offset. This is solution resistance. This offers an offset here and then it will predict that it will go vertically up.

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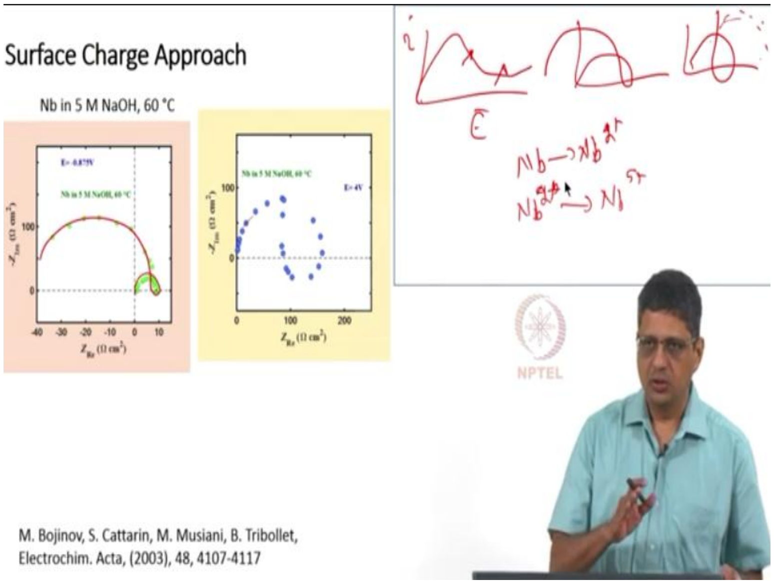

Surface Charge Approach

Nb in 5 M NaOH, 60 °C

M. Bojinov, S. Cattarin, M. Musiani, B. Tribollet, Electrochim. Acta, (2003), 48, 4107-4117

Another situation: Where you have niobium and sodium hydroxide, concentrated sodium hydroxide and a high concentration and at high temperature. It comes like this, the potential and current if I take poteniodynamic polarization, it should go like this. In the passive region, they see curve coming and settling here... This region goes up. Of course, [in] some of the example [experimental results], it actually goes here and then settles, but they are modeling only the part where it goes up.

It is possible to model this also… Fairly complex expression accounting for niobium becoming, I think Nb^{4+} or Nb^{2+}, I do not remember now, in the lattice. (I am sorry, not nickel, niobium) and then Nb^{5+} going into solution, Nb^{4+} going into solution or it could be Nb^{2+}.. if I …

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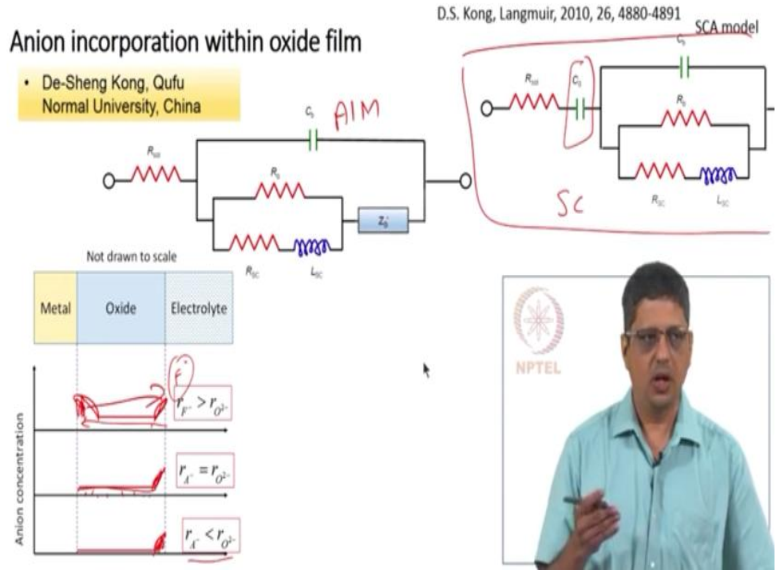

Anion incorporation within oxide film

- De-Sheng Kong, Qufu Normal University, China

D.S. Kong, Langmuir, 2010, 26, 4880-4891

There is another theory, which is called *anion incorporation* within the oxide film. This is proposed by De-Sheng Kong. So, the surface charge model says this is the behavior, of course with a capacitance here, okay. (I am sorry. *This* is the model proposed, *anion incorporation model*. *This* is the surface charge model, okay). The *surface charge model*, you may have seen that you have a C_0, which accounts for variation of film thickness with respect to the potential.

Another interpretation of the data is this, okay. This is usually seen when you have fluoride ion. We do not see this behavior, (I mean this inductive loop), usually we see this when we have fluoride ion, F^- ion. F^- ion is going to be very small, okay? and that is similar size as oxygen anion. So the interpretation is: In different situations, okay, (again this is not drawn to scale. They are considering only one film, not multiple layers). You can have anion. Anion here is fluoride ion, most cases the anion will come. It will not even go through the film. Some of it may occupy the location of oxide vacancies, but that is it. It is not going to move in. May be incorporated in the film solution interface… Near that location in the film it may get incorporated, that is it, not significant movement of this.

If the anion movement is smaller than the oxygen anion movement, oxide ion movement, then concentration of the anion is going to look little high here, decreases and then it is zero.

If that is comparable, then concentration will be non-zero, mostly it is going to be here, but near the film solution interface, it will be little high, but this is going to be non- zero, slightly above zero.

In case the anion movement is faster than the movement of oxide ion, they expect that it will move in and it will accumulate here, because anion is present to a large level, (fluoride ion may be present to a large level here) we will still see a slope here, to say concentration will be a little higher near the interface and lower here. But then it preferentially moves in this direction, because we have applied a positive potential, the negative ion will move and it will move faster than oxide ion. So, it causes an accumulation.

Now if you apply an AC potential, high frequency, it cannot keep up with that. It would not just move with the potential. At low frequency, it is possible [that these] anions will move to this side and this side and they are moving faster than what you would expect with the oxide anion. And his proposal is that this can cause… this can cause the behavior where low frequency it goes up.

So they take part of the surface charge model, they incorporate diffusivity here. This diffusivity or the mass transfer relates to the movement of this fluoride ion which are incorporated in the film, okay. So basically, at low frequencies, if you see a vertical line at low frequency and high potential… if you see a vertical line, in this complex plane plot and you see a mid frequency inductive loop. Point defect model does not explain that. Of course, this is seen in a very few restricted cases. Usually, with valve metals, usually with acidic fluoride medium.

Qn: Sir this is only for high DC potentials, right?
Ans: Yeah high DC potentials.

Inductive loop may come at low DC potentials, but it can be kinetic limited case. For example, I can get data like this,… I can get data like this. We can explain all those within the framework of mechanistic analysis. If you have a high rotational speed for the electrode, then you do not have to worry about mass transfer limitations and you might still see this. We have seen this before right. You can explain an inductive loop like this with kinetics.

Of course, you have to see whether it is realistic to explain for that particular case. See impedance spectroscopy gives you an idea about the system, but it does not tell you everything about the system. You will have to use other tools to augment this information. It is like saying if you do UV visible spectroscopy, if I tell you "At 500 nm wavelength, you have 0.3 absorbance", you cannot tell anything about. It can come from an inorganic salt. It can come from an organic dye. You will have to use other techniques to have an idea. And you can use this also, UV visible spectroscopy also. If you already know what is going to be in there, it is okay. If I give you an unknown solution, very dilute concentration, you put it in UV visible and you measure at one frequency or one wavelength, you really cannot say anything about it. You can just say it is pure water or contaminated. That is all you can probably say.

Even if you get over wavelength, you may not be able to say much about this, unless you identify few signatures. You will have to use other techniques to identify what are the compounds present, then to know the concentrations at different samples, you can use this, okay.

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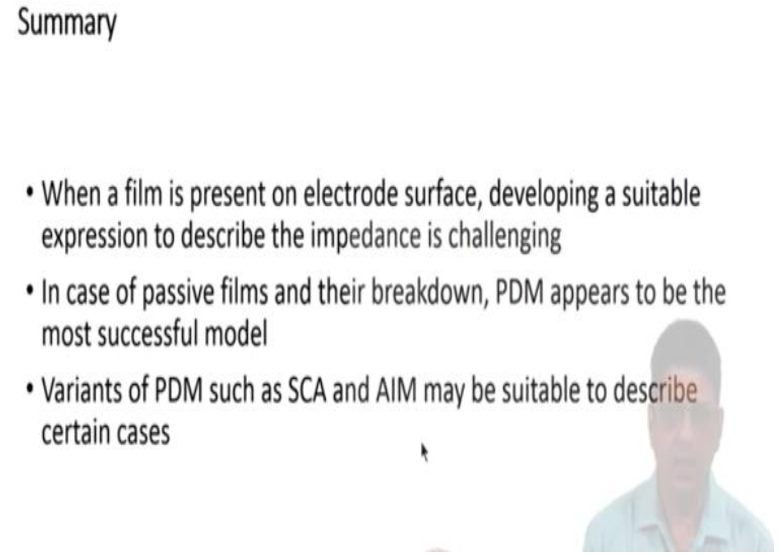

Summary

- When a film is present on electrode surface, developing a suitable expression to describe the impedance is challenging
- In case of passive films and their breakdown, PDM appears to be the most successful model
- Variants of PDM such as SCA and AIM may be suitable to describe certain cases

So, I will probably stop with this. So, in summary when a film is present on surface and when you are looking at the impedance spectra, it is not that easy to give a model for that. When it is for passive conditions, you can use point defect model. That appears to predict lot of these features successfully and explain the phenomena successfully.

In some cases, you may have to use variance of this, like surface charge model and anion incorporation model. These are alternate explanation, so SCA and AIM are complimentary, meaning both are aiming to interpret the same data. So, it is possible that the thickness varies with potential and that explains it. It is possible that anion is incorporated and that explains it. From my point of view, I cannot really tell which is a better model, okay, but these are proposed. So I want you to be aware of this.

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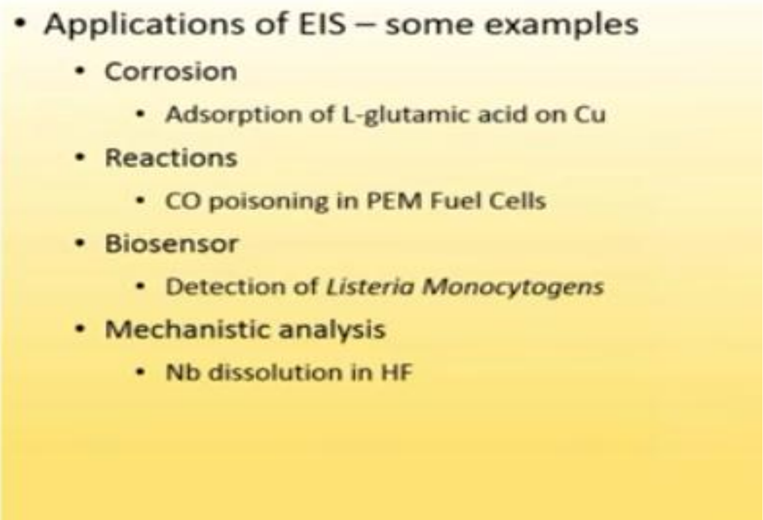

- Applications of EIS – some examples
  - Corrosion
    - Adsorption of L-glutamic acid on Cu
  - Reactions
    - CO poisoning in PEM Fuel Cells
  - Biosensor
    - Detection of *Listeria Monocytogens*
  - Mechanistic analysis
    - Nb dissolution in HF

What we will see next Tuesday is, few examples of what is published in literature, okay. We will stop here today.