Electrochemical Impedance Spectroscopy
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Lecture - 38
Films, 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
  - Surface Charge Approach

[Please refer to the video when the meaning of a sentence is not clear. Often, the instructor may point to something in the slide and refer to it as *this*. Watching the video would help understand the meaning better]

Today, I want to [show] how we can calculate the impedance, if we have a film on the surface. The film can be insulating or conducting. Conducting can be like a pure metal, can be like a semiconductor.

Initially, some models were proposed, which are fairly simple models. Later, for a film with passivation, which provides passivation, right. We have (what is known as) point defect model or PDM, with certain variations depending on whether it was earlier model or whether it was upgraded later. There are some variations of those, one is called surface charge approach and other is called anion incorporation model. So, we will see whatever is possible today and then continue tomorrow. Then I want to take up some examples of how EIS has been applied for few cases in the literature. So, one will be using equivalent circuit approach. Another will be using mechanistic approach. [We will see] may be one or two examples of these.

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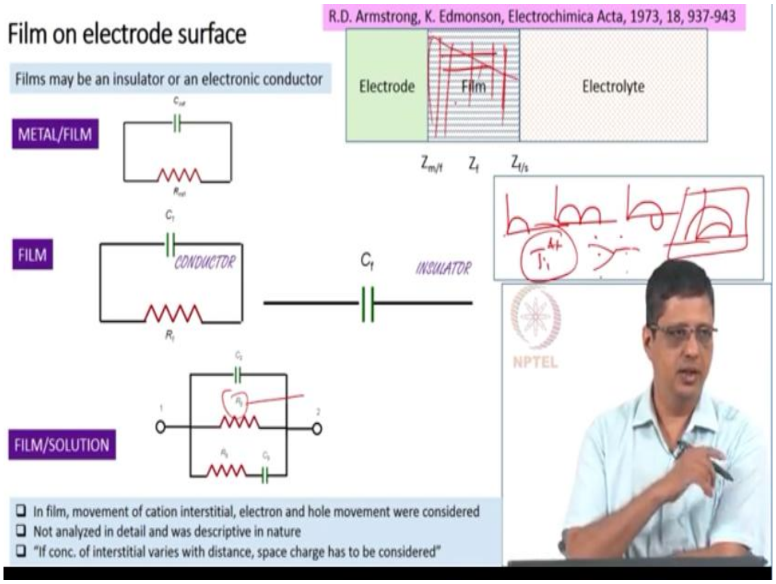

Film on electrode surface

R.D. Armstrong, K. Edmonson, Electrochimica Acta, 1973, 18, 937-943

Films may be an insulator or an electronic conductor

- ☐ In film, movement of cation interstitial, electron and hole movement were considered
- ☐ Not analyzed in detail and was descriptive in nature
- ☐ "If conc. of interstitial varies with distance, space charge has to be considered"

Earlier, Armstrong and Edmundson proposed the following picture for this. We have an electrode with a film and the electrolyte on the other side. We have a metal film interface. We have a film in between and we have film solution or film electrolyte interface and the impedance at $Z_{\text{metal-film}}$, Z_{film}, Z_{FS}, so he proposed a model for that.

[The] film can be an insulator or electronic conductor, electronic meaning it can have electrons or holes. Metal film interface was proposed to be modeled by a resistance in parallel with capacitance. Usually, a resistance is sufficient to model this, if the film is a conducting material. The film itself, if it is a pure insulator, it can be represented by a capacitor. If ~~it~~ [the film] is a conductor… but we are not considering pure metal, if it is a pure metal the metal *film* interface will be a simple resistor, probably [with an impedance] close to 0 Ω and the film itself will just be modeled as an electrode… [we are not considering a film which is an excellent electronic conductor, so a metal film coated on an electrode is not discussed here]…

If it is a clean film without any pores… . When we say conductor here, we mean it is an oxide, but it can conduct [electricity], like a semiconductor. It is an oxide, but not a clean crystalline oxide without any defect, but it has defects in it; and because of that, you have some conductivity. And the film solution interface, they propose that it can be modeled with this equivalent circuit. Assuming solution resistance is [negligible]. You have the C_2 here representing double layer capacitance.

It can possibly be only one resistance [in one example]. It can also contain a resistance and capacitance in parallel [to the resistance, in another example]. This is a Maxwell representation. You can have equivalent representation and other types of circuits, and allow~~ing~~ for negative values for all of these. That means, you can get only *this* [please refer to the video], if you have only R_2 along with C_2. You can get *this* [please refer to the video] type of behavior assuming all these elements have positive value.

You can have *this* [please refer to the video] type of behavior assuming R_3 and C_3 are allowed to have negative value. You can have this type of behaviour if you assume that R_2 can have negative value and of course when we have situation where we have passivation, the last one is likely to happen. But [all] these are simplified versions, and this was not analyzed in detail (in terms of getting [impedance] expression based on kinetic parameter, etc.), but are only described.

And ~~he~~ Armstrong and Edmundson considered that in the film, you can have electron and hole movements. You can also have (what is called) *cation interstitial*; cation here means, for example, if it is titanium oxide, Ti^{4+} is the cation, and you have a crystal structure; anything that goes in between [the lattice points], that is called interstitial. Anions usually do not move within this [film] as interstitial. And also, within the film, if the concentration of cation changes with distance, then space charge [has to be considered]. i.e., within the film if you slice it into thin volumes, then the total charge in each slice depends on the location of the slice. The space charge can also be considered; and at that level, the description was left without any further detailed analysis, [by Armstrong and Edmundson].

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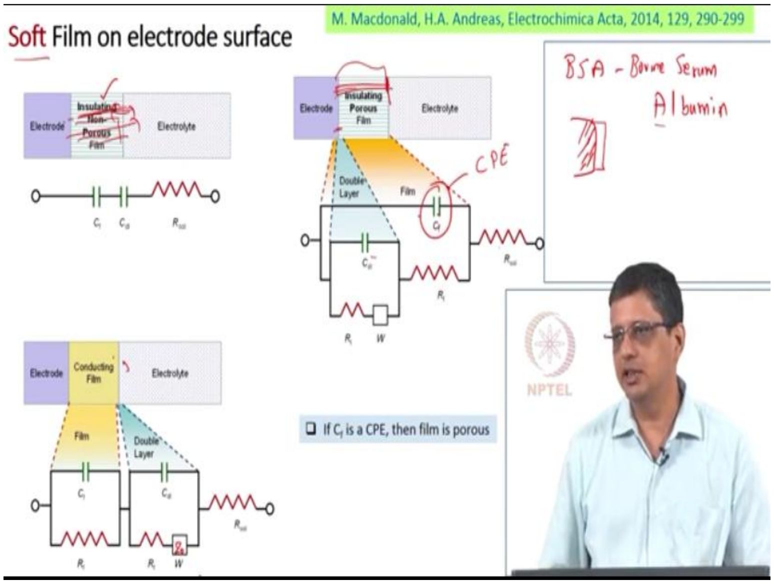

Soft Film on electrode surface

M. Macdonald, H.A. Andreas, Electrochimica Acta, 2014, 129, 290-299

❑ If C_f is a CPE, then film is porous

BSA - Bovine Serum Albumin

Recently, a group from Canada has proposed a set of equivalent circuits for soft films. This was specifically used for (what is called) bovine serum albumin or BSA, that is usually used in biosensors. BSA is a biomolecule. It is used to adsorb or block electrodes in certain specific cases. I will show you examples when I go to the applications later. When they analyze the adsorption of this BSA on gold or platinum metal, (I do not remember now, it is one of those two electrodes), they [suggested "if the film is insulating and nonporous, it can be represented by a capacitor "]. The film is supposed to be thin. It is a large molecule, but still it is not going to be, many nm thick. And that is represented by a double layer here, electrolyte here. Beyond this, you will not require ~~have~~ any element [to model this].

If [the film completely blocks the surface and] does not allow any reaction to happen, you are going to have C_{dl} and this. If ~~[~~reaction occurs], that means the film is porous with some liquid or electrolyte going in and touching this electrode. So, if you have an insulating film, but that is porous, it allows this electrolyte to *see* this electrode. We can represent this interaction between the electrode and electrolyte in the pore using this double layer structure.

You can say C_{dl}, R_t, and W (representing Warburg impedance or mass transfer). The overall film is still not very thick, so it is [modeled] by the C_f in parallel with R_f, and of course you have R_{sol} for the outside film to the reference electrode. This is [the circuit suggested] to represent an insulating, but porous film.

[The next example is this.] It is a conducting film, again it is a soft film. The way they have modeled that is to say “it is a capacitance in parallel with the resistance”. It offers significant resistance, it is not like a metal. It allows electron to pass through even if the film is an organic chemical, it can allow electrons to pass through to some [extent]. When the film is very thin, it will offer a resistance, but [the resistance] is not infinite. And then from here, there is a reaction. So the reaction occurs here that is given by this R_t and W. W [Warburg impedance] may or may not be present, depending on whether you have mass transfer limitation or not.

So this is more general and if you do not need Z_D [to model the data], you can remove that from the circuit, but you cannot just [visualize] that this entire thing is an electrode. You will have to add a capacitance and resistance for this. So, for example, you may deposit a film on an electrode and that may catalyze a reaction. If it is very thin film versus a little thicker film, you may see a change *here* [please refer to video], although *this* [please refer to video] may not change. So that is one way to look at this.

But these are still a macroscopic representation saying that, “You have a film, I am going to model this by capacitance [and] resistance [and so on]. I am going to model *this* by a capacitor. I am going to say this is porous and then I put a Warburg impedance for this”. And they [the authors] also made a comment [saying] that C_f is a CPE; i.e. if you model *this* [please refer to video], it comes out as a constant phase element, that it is modeled better by a constant phase element than by capacitor; if you actually model *this* [please refer to video], you are not able to model the data well, if you use capacitor, but you are able to model the data if you use a CPE, then, [in that case] it is quite likely that this [film] is porous. That is one of their comments.

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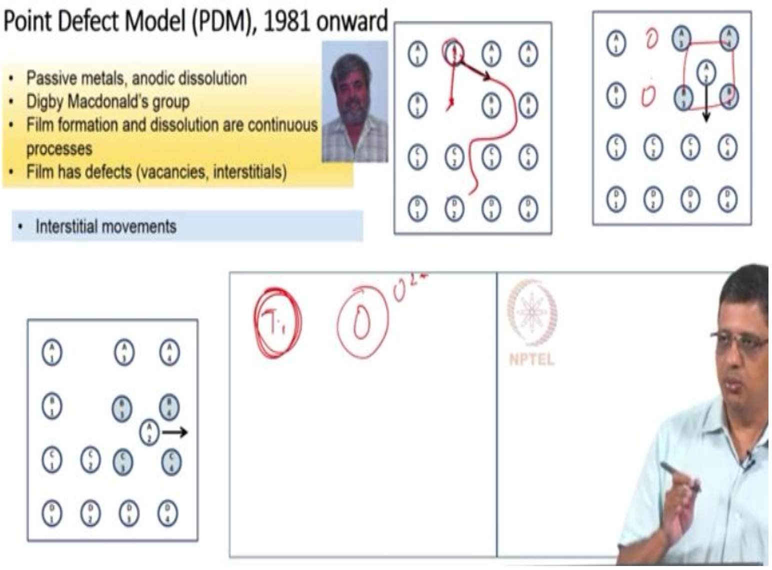

Point Defect Model (PDM), 1981 onward

- Passive metals, anodic dissolution
- Digby Macdonald's group
- Film formation and dissolution are continuous processes
- Film has defects (vacancies, interstitials)

- Interstitial movements

A more detailed model for passive metal [was given later]. Passive metal means metals which offer passivity in [many] solutions, [metals] like tungsten, aluminum, titanium ; even normal metals like nickel, which offer passivation in ~~lot of~~ [many] situations. How do they, [these films] respond to AC perturbation? What impedance would we see if I apply AC perturbation on that [passive film]? And this is modeled in detail [unlike the previous ones we saw].

So, I want to go through the steps; NOT the entire derivation, [because the] derivation is very lengthy and complicated; but [I want to illustrate] what is involved in coming up with the model, what are the steps that are necessary [to describe the processes occurring in the film]; and qualitatively what one would expect to see [in the impedance spectra]. From these mechanistic steps, one can say, “This is what I would expect to see in the impedance”, .

First, is the film, which is present; on one side you have a metal, [and on] another side you have electrolyte. The film is not a proper crystal. In general, it is amorphous; or it can be [made of] many small crystals, polycrystalline. It will have lot of defects. Defects means, for example, vacancies or interstitials.

So, I want to show you [an example of the] movement of [an] interstitial. If you assume *this* [please refer to video] is a lattice in 2D, *this* is a vacancy. Of course, when there is a vacancy, it is likely to move there, but right now, [let us] ~~we~~ just pretend that this schematic is fine.

This location, [the] atom in *this* location *A2*, if it moves *here*, it is going to cause a strain in these 2D, of course, in 3D it is going to be in all the atoms surrounding that. When it moves NOT through the lattice location, (so you have a vacancy here, you have a vacancy here), but through a gap between [the lattice points], that is called interstitial movement, .

Cations: if I take e.g. titanium, they lose electrons. The size of a titanium ion is going to be slightly less than the size of [Ti] atom. On the other hand, if I take oxygen the anion O^{2-} is going to be little larger [than an oxygen atom] .

Within this film, the cation is not going to be hydrated. If I think about solution, in the electrolyte, [a] cation is going to be surrounded by water dipoles; whereas, within the film, it is not likely to be [surrounded by water molecules]. Water is not likely to be present inside [the film]. So, [the size of a] cation is smaller here [in the film].

In the electrolyte, cation tends to be small, but [a] cation does not [move] alone, it is always surrounded by water dipoles. Therefore, it ends up being actually large [in size]; meaning, the cation plus the water dipole structure (sheath around that), they move together. Therefore, this group is large compared to anion [in electrolyte].

So, anion does not usually move within [a] crystal [i.e. film]. It is very hard for a large ion to move through the crystal. It can hop, meaning an anion *here* can go to the vacancy, [that is] no problem. But it cannot go like *this* [as interstitial]. When I say “it does not move”, I mean “it does not move as an interstitial”. It , [the anion,] can move to [fill] vacancies in [the] lattice.

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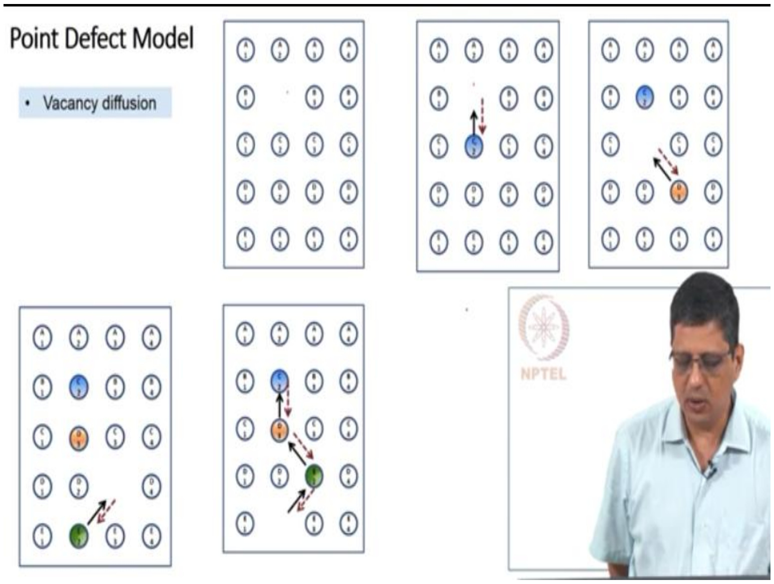

Point Defect Model

- Vacancy diffusion

Now [we consider] diffusion of [a] vacancy: In this example, let us say, first the atom or ion… in location C2 moves to the vacancy, which is in B2. B2 is not [filled] here, that is a vacancy now. So, I can say “C2 moves to location B2”. [Alternatively,] I can say “The vacancy moves from B2 to C2”. So the vacancy movement is shown by the dash brown line. Next, let us say that “D3 moves towards the vacancy in C2”. Next, I can say “E2 moves towards *this*”.

So. what this means is, I can say that “there are multiple anion or multiple ion movements” or I can say “One vacancy is moving here”. So, it is like this: if one of you move to [an] empty location, another person moves *here*, another person moves *here*, another person moves to that empty location… It is basically shifting of many different individuals by one unit [this is vacancy movement]; versus, a person walks in, moves in between and then comes and sits, *that* is interstitial, .

I can think “Many different individuals, jumping or moving [by one unit distance]”; or I can say, “One vacancy is continuously moving”. So, this is one vacancy, continuously moving. That is how we want to describe it here. So what it means is: Cation can move ~~via~~ as interstitial; cation can [also] move via vacancy mechanism; [but] Anion will not move as interstitial. [Anions can move only via vacancy movement inside the film].

So if anion comes on *that* side, (let us say *that* is film solution interface, *this* is metal film [interface]), this entire region is covered with film,… That anion is not likely to come all the way *here* that easily, although that anion can fill a vacancy. A vacancy jump can happen, i.e., if there is a vacancy here for anion, another anion can move here, another anion can move to that [location] etc., so it can accommodate a fresh anion from outside, although vacancy was originally *here*. The vacancy has to jump many times, go *there* [to the film solution interface] and then the fresh anion can be accommodated there. Although vacancy is *here* [at metal film interface], it is not possible for that anion [at the film solution interface] to just walk right through [the film, as interstitial] and come here [to the metal film interface and fill the anion vacancy].

Whereas if cation vacancy is there [at the film solution interface], a cation can go through this lattice [as interstitial], cation can also go via jump; jump meaning "via lattice jumps" [i.e. cation vacancy movement, and fill the cation vacancy at the film solution interface].

So essentially, I can summarize *this* [illustration] as "Three ions moving", or I can say "One vacancy moving by three steps"; three ions move by one step [each] or one vacancy moving by three steps.

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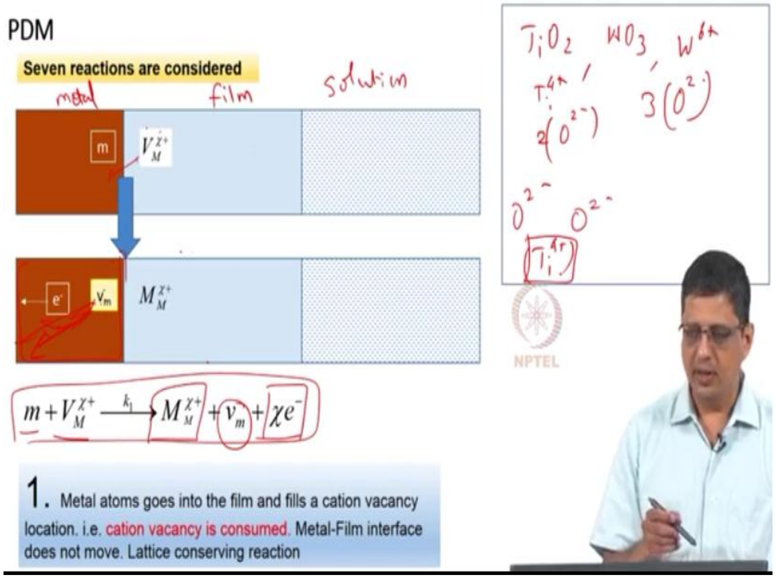

PDM

Seven reactions are considered

$$m + V_M^{\chi+} \xrightarrow{k_1} M_M^{\chi+} + v_m + \chi e^-$$

1. Metal atoms goes into the film and fills a cation vacancy location. i.e. cation vacancy is consumed. Metal-Film interface does not move. Lattice conserving reaction

So this is the description here; You have a metal on one side, solution on the other side and [a] film in between these two. You have a metal. On top of metal, you have a film and that is exposed to the solution. To a large extent, I will use a notation that is used by the author, (i.e. Prof. DD. McDonald), but some cases I will probably use a slightly different notation.

So, totally there are 7 reactions that are considered here. First reaction: You have a metal, and in the film, there is a vacancy for the metal; and the metal is present in the charged state [i.e. it is a cation]. ~~It is~~ [The vacancy is actually] a vacancy for the ion.

Film, (for example may be TiO_2, it may be tungsten oxide,) here it is present as Ti^{4+} and two O^{2-} ; W^{6+} and three O^{2-}. Now, here in this example, you have an anion or you have two anions, [one] O^{2-}, [the second] O^{2-} and we are expecting [a] Ti^{4+} to be present [here], but that is not present here, it is a vacancy. [Therefore, this] is a defective film. ~~So~~ That vacancy is in charged state; if that [vacancy is to be] filled, it has to be filled in charged state [i.e. by a cation, and not by a neutral atom or by an anion].

We cannot replace this with a titanium atom. (It has to be replaced), it has to be filled by a Ti^{4+} ion. So, what happens is, *this metal goes as ion here*, it leaves a vacancy here, for the metal, 4 electrons are taken here. This χ here represents 4 in this example, it can represent 6 for tungsten, whatever that charge [of the cation] is. *This* is vacancy in the metal. *This* is ion in film, and *this* ion is going to be right next to this metal film interface. It is not going to replace a vacancy *here*.

If it has to replace a vacancy *here*, it needs multiple jumps [to get] there. So, in one step, all that we say is "[At] metal film interface, any vacancy that is right next to this interface, any vacancy in the film right next to this interface, can be filled by metal going to *that* with electrons transferred into *this*". The vacancy within the metal is usually taken up quickly, (meaning it moves quickly), metal atoms will come and fill this very quickly, it [i.e. the vacancy] is taken in, [well inside the metal].

So, we assume [that] we have a bulk metal, [then a] thin film on the surface, [which is] exposed to the solution, and any vacancy that is generated in the metal will quickly go in[side the metal].

So, we have a large sink for this [cation vacancy inside the metal]. We say “it is consumed quickly”. So, the equation is written like this: First reaction, is k_1 occurring at rate given by this, [here] k_1 is the rate constant. Metal near the interface plus a cation vacancy, near the interface, they interact. The cation vacancy is filled in the film. Vacancy ~~is~~ ~~put in~~ [moves inside] the metal, (but it goes quickly), it disappears quickly and χ number of electrons are released.

Qn: “The quick reaction is the vacancy in the metal getting consumed?”

Ans: “That is assumed that it is very fast. See, this vacancy [in the metal] is not going to remain here. So, what we assume is, *this* [step, i.e. cation vacancy getting filled by metal atom] is a slow step, (possibly a slow step). What we show here is a slow step. What I am describing (and not showing in the picture) is, *this* [cation vacancy in the metal] moving [inside] quickly. So, what will happen is, *this* side is going to be replenished like *this*.

After this, implicitly I am going to say, *this block with the vacancy* is going to look like *this block without vacancy*. Because this vacancy is filled by metal atoms moving in; *metal atom moving in* is considered very fast”.

So what we say is, “In the metal film interface, the cation vacancy is now consumed”. This interface does not move. We still have metal on the left of this interface and film on the right side and this is called *lattice conserving reaction* .

Overall, there is a dissolution of the film. Under state condition, if you just have a DC potential, you will have a film of certain thickness. *Steady-state* does NOT mean [that] nothing is happening. What it means is “The rate of dissolution of the film should be equal to the rate of formation of the film”. Then the film thickness will remain the same. That means, its interface is moving continuously, but it is retaining this thickness (on the average, of course).

Qn: We are not making a new cation vacancy, we are just consuming that vacancy, so how it is it possible that we are maintaining the interface”

Ans: So there are 7 reactions, we are still describing the first reaction”

Qn: “But in that you have mentioned na, that we have to maintain that interface”

Ans: “So when we see all 7 reactions….[it will become clear]. I have not described the dissolution of the film yet. I have not described the formation of the film yet. So, when we see all 7 reactions, we have to put [all of] them together; and then, we should expect [that] under steady state conditions, the rate of dissolution and rate of formation of the film have to be the same. Here, in this example or in this step, we are not forming film, we are not dissolving film, we are filling the vacancy in the film. So this is not going to increase or decrease the thickness of the film.

Second step…So, in this of course, you have lattice points, right? Some of them may be filled, so some of them are going to be anions, some of them are going to be cations, that is [the] first point. Second point, some of them are going to be vacant. It can be [an] anion vacancy or [a] cation vacancy. If it is a cation vacancy, only a cation can fill it; [and if it is an] anion vacancy, only an anion can fill that.

Also there are gaps in between [the lattice point locations]. So, a metal near the interface, metal on the left side [of the interface] can lose electrons. It can go into *this* as an interstitial. Cation can form [and] if there are no vacancies right next to *this*, if all these [lattice points] are filled with cations and anions, with no vacancy, still it is possible for this metal, (when we give positive charge [to the electrode], when I make it anodic, when I make this *electrode* anodic), it is possible for the metal to lose N number of electrons or χ number of electrons, become $M^{\chi+}$; if there are [cation] vacancies, naturally it will first go and fill the vacancy. [If there are] no vacancies, [then] it can go as an interstitial. That is the second step.

Again, the vacancies that are formed on the metal side are consumed quickly. Therefore, the metal remains as one block. The one on the left side [is not changed], film also remains [the same] on the right side, [so] it is a lattice conserving equation, and of course we call the rate constant as k_2.

Qn: If the film has vacancies, obviously the preference will be first to, fill the vacancies, then it goes into the interstitial, [isn’t it]?”
Ans: Yes, at least that is what I would guess. ,

Qn: So, there is obviously a preference, right?

Ans: Yes.

Qn: So the equations …. [should reflect it, right?]

Ans: Yes. So when we assign rate constant, we should look at the data and see which one happens,… and I have not gone into the details of analyzing an experimental data with this [model yet]. But if I have to guess, I would think [that] cation vacancy will be filled preferably and if there are no vacancies, only then a cation would go towards interstitial. Or if it is going to go in both [vacancy filling and as interstitial] simultaneously, in parallel, I would say [that] for filling the vacancies the rate constant would be larger and for going towards interstitial, the rate constant would be smaller.

Qn: Sir if it was a cathodic potential, will it happen?

Ans: [At] cathodic potential, you would not have a film formation. If a film is already existing, then the film will be there. It is not easy to reduce certain films. Some films can be reduced and some films may not be reduced, but typically you will also not have film dissolution… under cathodic condition, you would not have significant film dissolution. So nothing will happen, that is all.

Under anodic potential, this [film dissolution] can happen. Under cathodic potential, for example, in corrosion, people use what is called *cathode protection*. So, they will apply a negative potential, and as long as it goes [the potential is maintained] below certain value, you will not have this [dissolution]. If you go too negative [a potential], you may have other problems, but that is a slightly different story. If you are [going] too negative [in potential], hydrogen evolution will happen and that will lead to other issues. Generally, here, we are considering anodic conditions. So is this part okay?

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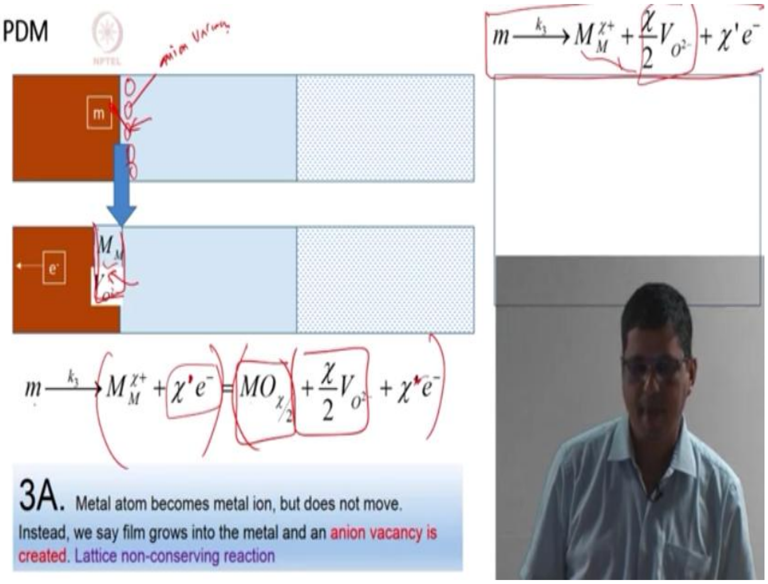

$m \xrightarrow{k_3} M_M^{\chi+} + \frac{\chi}{2} V_{O^{2-}} + \chi' e^-$

$m \xrightarrow{k_3} M_M^{\chi+} + \chi' e^- = MO_{\chi/2} + \frac{\chi}{2} V_{O^{2-}} + \chi' e^-$

3A. Metal atom becomes metal ion, but does not move.
Instead, we say film grows into the metal and an anion vacancy is created. Lattice non-conserving reaction

Third, what is given… (the equation is written like this), a metal near this interface. It does not go as interstitial, it does not fill any vacancy, because probably there are no vacancies around here or there are not too many vacancies. It loses N number of electrons or χ number of electrons; χ number of electrons, and becomes cation, but it has not moved yet into the film.

Instead, …(what we say is the following) Let us say, there is an anion vacancy here. *This*, we can say, is associated with this cation; and together it forms, “film + an anion vacancy”. Instead of saying it is just a cation, we say it is a film, which is metal oxide, with an anion vacancy. That means film is going into this metal. That means, anions will diffuse in, by single jumps and come *here*, if not immediately after this [anion vacancy formation], probably few moments later. Anion will come *here*, sit next to the cation, it forms a metal oxide film.

So the way I have written, i.e. metal with a rate constant k_3 forms a metal ion, (cation), by giving up so many number of electrons, and that is equivalent to saying “You have a metal oxide film with [an anion] vacancy”. Of course, you are giving up the same number of electrons as before. So, I can say “*This* on the right side” or I can put this on the right side. The way it is written, i.e. “it forms a metal cation, and it is associated with a vacancy”. So this is describing (probably implicitly) that this is actually a ~~metal~~ film. It is NOT a metal cation sitting in the metal. (If it is a cation, it cannot be in[side] the metal. [A cation] has to be in the film, or it has to be in the solution. An atom is in the metal; an ion is not in the metal. Neither an ion vacancy nor an ion [can be] in ~~the~~ metal. So, this way, it is a film forming reaction, so we say “Metal atom becomes a metal ion, but it has not moved into the film, existing film yet. So we would say “It is film growing into the metal” and we also say “[An] anion vacancy, (an associated anion vacancy) is present”. And this is called [a] *lattice non-conserving reaction*, because lattice actually grows. This is the third step.

Another way to visualize this [shown in this slide]; it is effectively the same reaction. So, we can say “*These* are all cation and anion, filled cations and anion locations in the lattice. When a metal loses a number of electrons and $M^{\chi+}$, an anion *here* can move next to *this*, leaving a vacancy *here*”. Then you can clearly see [that] *this is a metal oxide*. That is also possibility. It is just another way to visualize this to say, “We are forming a metal oxide here, with [an] oxide vacancy”. So, I can say “This oxide vacancy is in the film that is already present” or I can look at it in the previous [slide] and say “*This* cation is formed and that is associated with the vacancy”.

Either way… You can visualize this either way, but basically this is metal forming film by losing *N* number of electrons.

Qn: Does the oxygen come from film or within the metal?

Ans: There is no oxygen within the metal. The oxygen has to come from the film. Oxygen actually has to come from outside through the film, but it does not just diffuse and come in. It has to come by multiple movements of oxygen anions, [oxide] ion, or the corresponding vacancies.

Qn: So, this vacancy, (anion vacancy) is created in the film, is it?

Ans: ~~So~~ One way to visualize is this: One anion that is already present in the film has moved here, but that is going to leave a vacancy for anion.

So, here, we are generating anion vacancies. Look at the previous cases. Let us look at it one by one.

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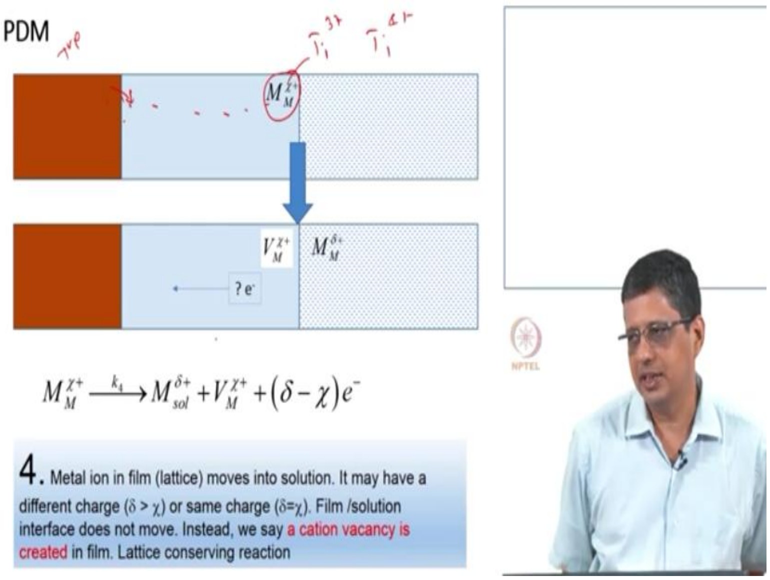

PDM

$$M_M^{\chi+} \xrightarrow{k_4} M_{sol}^{\delta+} + V_M^{\chi+} + (\delta - \chi)e^-$$

4. Metal ion in film (lattice) moves into solution. It may have a different charge (δ > χ) or same charge (δ=χ). Film /solution interface does not move. Instead, we say a cation vacancy is created in film. Lattice conserving reaction

First, we are consuming [a] cation vacancy, that means somewhere else, I have to produce cation vacancies also; but right now, we are looking at [this] step by step [and will look into the production of cation vacancies a bit later]. One, we are consuming cation vacancy *here*. *Here*, we are not producing any vacancy, we are not consuming any vacancy, we are just producing interstitial. Interstitial has to be taken out somewhere also [and that step will be discussed later]. That is also there. We are producing interstitial in the second step.

[In the] third step, we are producing anion or [oxide] ion vacancies in this example. And there are multiple ways to describe that or visualize it.

Qn: Sir, but in the metal electrode, there would not be any vacancies, because outside there are some…

Ans: [Yes, In the] metal electrode, there would not be any vacancy. So, if we see a vacancy here, it is not metal. If we see a vacancy right next to that, metal cannot be present as an ion. So you have an ion *here*, you have a vacancy, it has to be a film.

Qn: Sir, but the oxygen ions are coming into the metal, I mean, at the interface and forming oxide right?
Ans: Yes

Qn: It is like a layer is growing inside.
Yes.
Qn: For that to happen, there should be some vacancy in the metal electrode right? Otherwise, how will the oxide formation happen?
Ans: There is going to be expansion of the metal. When metal is oxidized, its, it is not going to remain at the same volume. It is going to cause a strain. We are showing it like a clean colour. If there are atoms, [and] oxygen comes in, it is going to strain *this*.
Qn: But anions, obviously anions cannot…
Ans: Anions can move one jump if there is a vacancy.
Qn: They can, (how do we say it), move through vacancies, but they cannot move through interstitials, right?
Ans: No, they cannot. OK, just visualize this, let us say *this* is a imaginary plane. We have metal *here*, another metal *here*, another metal here. *This* metal loses an electron, It becomes an ion. *This* also loses an electron becomes an ion. *These* are positively charged; negatively charged material will be attracted towards *this*. Anion will come in, [now] don't think of it as an interstitial ~~now~~, but it is pushing it apart and coming in. That is forming the film. So, when a film is formed, (oxide is formed) on a metal, there is going to be a strain.

Now, one can argue and say "that is coming as an interstitial", but one more layer is formed, *this* moves in, *this* is actually film with different gap between the metal atoms. So, between the metal atoms, there is a space. In the pure metal, there is going to be one [value for the interatomic distance]. In the oxide it is going to be larger space, between the ~~metal atoms~~ [cations], because it is going to be metal, (oxide), oxygen, metal.

That comes because of *this* [oxygen] coming in, and pushing it out. There is going to be strain. There is going to be stress associated with that, but we do not call that as interstitial movement. But ... I suppose your question is, "you have a metal here, you have another metal atom here, how are you getting a vacancy, is it called interstitial?". No, We do not call that interstitial… and when an [oxide] anion comes here, it is going to push this metal atom outside, inside, whichever way you describe it, but we call it as formation metal oxide there.

Qn: So through the film, it hops through the vacancies, but when it comes to the interstitial…"
Ans: It forms oxide. It pushes them out and forms oxide.
So that is going to cause a strain, but we do not call that as [insterstital]. …. Interstitial.., To be called truly as interstitial, it has to go through many, many such layers or many such planes freely. Then it would be called interstitial; whereas, here it comes, pushes it out and stays. At the most, it can move one step. It can't move multiple steps, (or, we do not think it moves multiple steps).

Qn: "So, for the happening or the further growing of the film into the metal electrode, there will always be a constraint because of the strain, right?"
Ans: Yes. See basically, let us say, this is metal. It has formed a cation. *This* you may have another metal also present here forming a cation and oxide anion here will move here and leave a vacancy.

Now *this* metal can form a cation after some time. *This* can move *here*, so that it is associated with that. It will leave a vacancy *here*. One way, you can think is "When it forms a cation, it forms a vacancy, right next to that; and therefore to fill that vacancy, it is moving in". That is one way to visualize it; But whenever this metal gets converted to metal oxide, it is going to cause.. at that interface, it is going to cause a strain.

In fact, when it is continuously forming and growing, it has lot of stress; that is why this film is not crystalline, or it is not really large crystal. You can have small crystals, but [by and large] [the film] is amorphous,

Next, we want to look at the interface of the film and the solution. So here, there is a metal cation present in the lattice and that can go into the solution. Of course, we say it is positively charged, right. So, it is likely for the metal cation to go out into the solution. In general, this may be present as Ti^{3+} for example, and in the solution, it may be present as Ti^{4+}. Many a times, so we say *this* is metal; *this* metal cation present in the film, going into a solution, with possibly a different oxidation state. If δ and χ are equal, then there is no electron transfer involved in this. It just goes into the solution and leaves a cation vacancy.

This is the *generation* of cation vacancy. In the first step, we consumed a cation vacancy. This step generates a cation vacancy. If necessary (if this χ and δ are different), electrons will be transported through this, it will produce electron; if they [χ and δ] are the same, there would not be any electrons [transferred during this step]. [If] there is an oxidation involved in this reaction, you will have electron. So naturally when you look at the impedance calculation, you have to consider this as a Faradaic reaction. If δ is same as χ, we just say "It is a chemical reaction".

So, metal ion in the lattice moves into the solution, it may or may not have the same … charge. When it moves, we still say "The anion associated with this is present [in the film]. The film does not change in the length or size". We just say "[A] cation vacancy is created in the film". Cation vacancy is created in the film, it will diffuse through the film, come *here* and *this* first step will fill that vacancy.

So *this* step and the first step do not change the thickness of the film or length of that film.

Qn: Combing the step 1 and 4 will not change the thickness?
Ans: Individually, they will not [change the film thickness], combining them, we will not [change the film thickness]. [By] combining them, you will have a mass balance for cation vacancies. One [step] generates cation vacancy, another [step] consumes cation vacancy.

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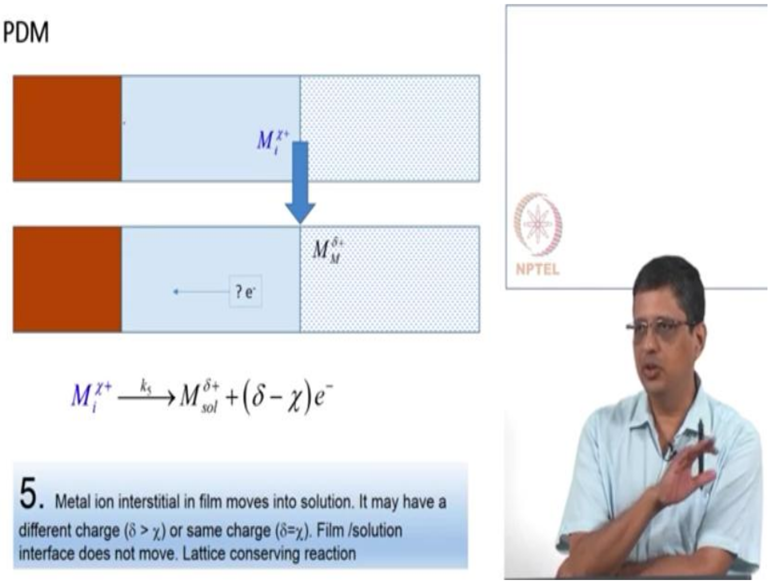

PDM

$$M_i^{\chi+} \xrightarrow{k_5} M_{sol}^{\delta+} + (\delta-\chi)e^-$$

5. Metal ion interstitial in film moves into solution. It may have a different charge ($\delta > \chi$) or same charge ($\delta=\chi$). Film /solution interface does not move. Lattice conserving reaction

OK, [an] interstitial can also go into the solution. Interstitial, at rate constant given by k_5, can go into the solution. So it is a pretty straight forward reaction. It was not really present as part of this lattice. When it got generated from the metal, it went in between *this* and then went out of *this*. Basically, in some sense you can say interstitial generation, interstitial consumption, they are in general of course, going to be equal, ~~but~~ under steady state condition; but ~~it~~ [this step] is not going to form or consume the lattice.

Interstitial can also fill the cation vacancies, right? We are not considering them. Likewise, a cation within the film can move into interstitial, [it is] not likely to happen, we are not considering them. Usually if there are no cation vacancies, if a film is of particular nature, certain nature, such that there are not many vacancies, cation sites are also filled; anion sites are also filled; *then* it is likely that this cation interstitial is the (main movement), main transportation pathway.

So in general, we are considering all the reactions. It is possible that for a particular case, only certain type of reactions are dominant. So, formation of [a] cation vacancy and transportation of [a] cation vacancy and consumption of [a] cation vacancy may be a dominant mechanism in a particular metal oxide case. Another case, [movement of] cation interstitial may be the dominant mechanism [of current transport].

Another case, anion vacancy [movement] may be the dominant mechanism [of current transport]. Anion interstitial [movement] is not likely. So, we are considering all these equations, but it does not mean [that] in general, for all cases, all of these steps will necessarily be of equal magnitude or [of] comparable magnitude.

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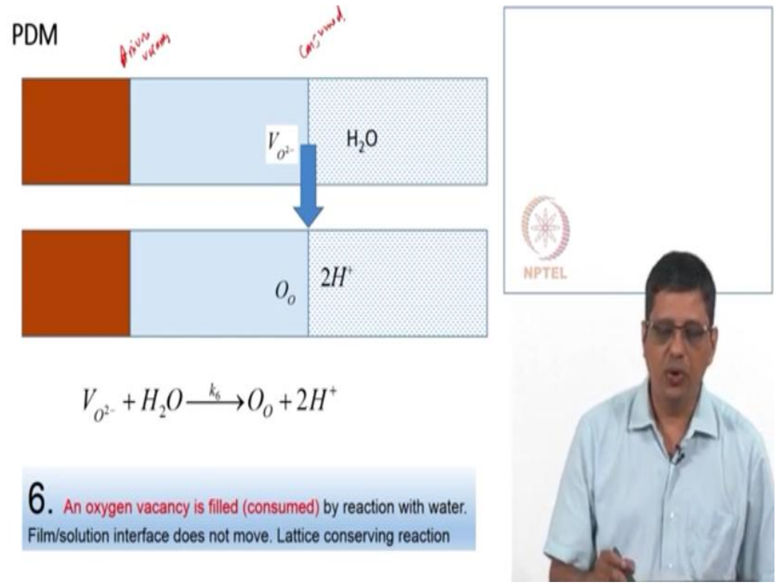

PDM

$$V_{O^{2-}} + H_2O \xrightarrow{k_6} O_O + 2H^+$$

6. An oxygen vacancy is filled (consumed) by reaction with water. Film/solution interface does not move. Lattice conserving reaction

The next one is consumption of anion vacancy. In the early step, second step anion vacancies are produced at this location and they are consumed in the 6th step, we show that they are consumed in this location. If you have an anion vacancy here, that can be filled with oxygen and oxygen comes from water. So, water, reacting with this film…, so basically anion vacancy means, there is a cation right next to that, there is no anion, sees water, it is going to grab the oxygen and release the H^+, .

Qn: There is a competing reaction in the previous slide?

Ans: Previous slide is interstitial going into this.

Qn: One of the older slides were V^O was there?

Ans: No, ~~no,~~ it is not competing. *This* is the one [you are referring to], right? [Step] Three; Formation of V^O. Whenever cation is formed, we say oxygen vacancy is formed. Whenever cation is formed in the metal, it is no longer a metal, it is a film with oxygen vacancy.

When a cation is formed and fills the vacancy right next to this interface in the film, we just say it is filling that vacancy. Film is not moving. It is not growing. When it goes to interstitial, no problem. When it becomes a cation, it cannot go and fill any vacancy, it cannot go as interstitial, this is actually film formation with anion vacancy.

So, that is production of anion vacancy. In this case, we are consuming the anion vacancy. So *that* reaction has to balance *this* reaction, if this is the dominant mechanism. If movement of anion vacancy is the main way to transport current, film formation, film dissolution… Under steady state condition, when you look at this, whenever you are creating [an] anion vacancy, you also have to consume [it] at another place. We are creating anion vacancy at *this* location, [and] consuming [it] at the film solution interface.

Complimentary: Cation vacancies are created at *this* [film solution] interface and they are consumed at the metal [film] interface. So, we say "Oxygen vacancy in the film is filled or consumed by reaction with water". Again 2 H^+ go into solution, the oxygen has come here, but the film has not moved yet. So, it is again a *lattice conserving reaction.*

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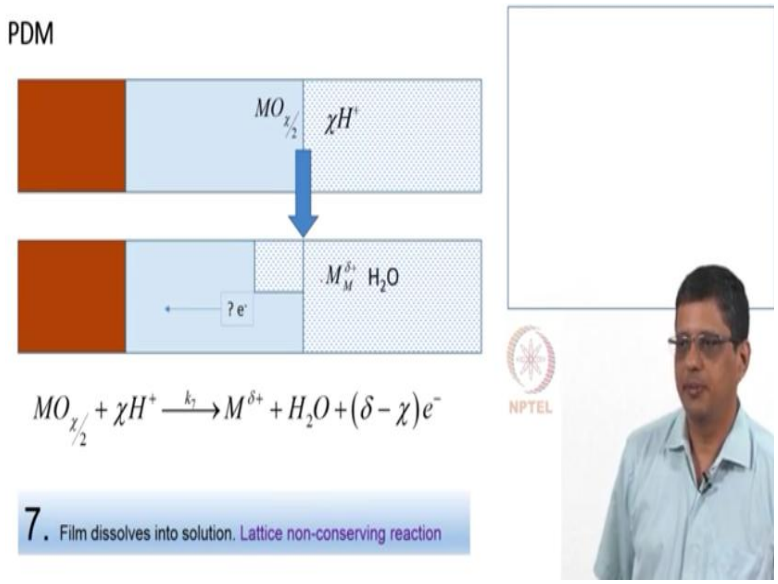

PDM

$$MO_{\chi/2} + \chi H^+ \xrightarrow{k_7} M^{\delta+} + H_2O + (\delta - \chi)e^-$$

7. Film dissolves into solution. Lattice non-conserving reaction

And the last one is film dissolution. Metal oxide, I have given it as $\chi/2$, but basically it depends on the valency of this metal. If it is 4+, if it is Ti, we will write it as TiO_2. If it is tungsten, we will write it as WO_3. If it is tantalum, you will write it as $TaO_{2.5}$ or Ta_2O_5. That in presence of H^+ ion (typically anodic dissolution occurs in presence of H+ ion, [and in] acidic conditions)…

So metal oxide becomes metal [ion] in the solution phase, [a] cation in the solution phase. H^+ and $O^{[2-]}$ form water, and if there is oxidative reaction, you will get an electron, otherwise you would not get electrons. Basically, film is ~~gone~~ [dissolved]. So, this is film dissolution. And this is (naturally) *lattice non-conserving* [step].

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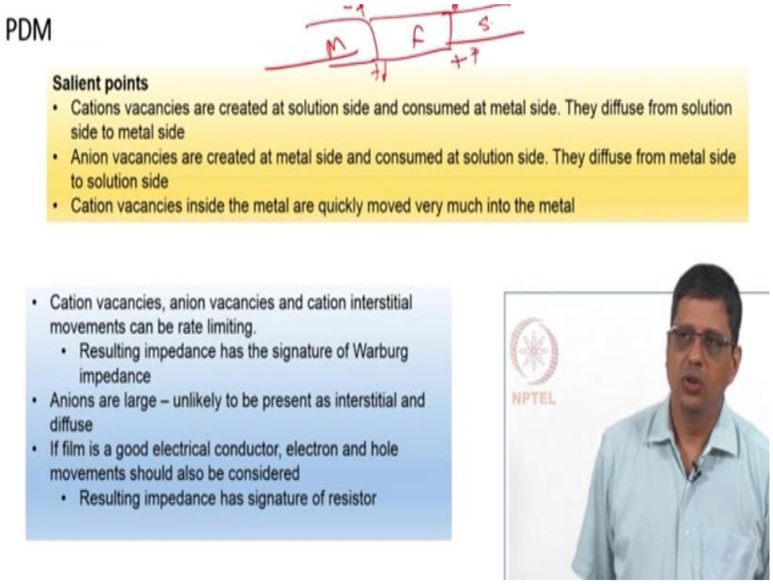

PDM

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

So [note a] few points: Cation vacancies are created on the solution side. [We have] metal… film… solution. Cation vacancies are created *here*. Cation vacancies are consumed *here*. Anion vacancies are created *here* and anion vacancies are consumed *here*. Cation vacancies in the metal go quickly in *there*. Anion vacancies [are] consumed *here* using water. So, water is of course replenished. It is a liquid. The moment it gets consumed, it is going to be, another water molecule is going to…[come to that place].

In general, the film also ~~will~~ [can] have electrons and holes; CAN have electrons and holes. If we say that the vacancies are moving, or interstitials are moving and they are the rate limiting step. You can derive ~~it~~ [the equation for impedance], it will have a signature of Warburg impedance or something similar to that, because diffusion is rate limiting. Diffusion here occurs in the presence of electric field.

Diffusion of charged species, so it is not just Fick's law. You have to use additional factor accounting for the movement of the ions in the electric field. So, when I say "It is going to *sort of* look like mass transfer limited case", in certain cases, it will look like Warburg impedance with a finite boundary layer thickness. Anions are large, therefore they are not going to move as interstitial. And if the film is actually a good electronic conductor…Electrons and holes move very fast, (compared to the movement of these ions by diffusion). So *this* [diffusion of cation and anion vacancies or cation interstitials] will not give that much current [compared to the current carried by the electrons and holes]. The maximum current will come because of the flow of electrons and holes. So it [the impedance signature] will look pretty much like a simple conductor.

So, platinum oxide for example, (if platinum can form oxide on this, but) it is a very good electronic conductor. You will not see any of this behavior, the Warburg like behavior [if we have a platinum oxide film on top of platinum].

We will continue with this tomorrow.