Indian Institute of Technology Kanpur

National Programme on Technology Enhanced Learning (NPTEL)

Course Title
Manufacturing Process Technology – Part- 2

Module- 18
Electrode Double Layer

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Hello and welcome to this manufacturing process technology part 2 module 18 we were discussing about how the potential at a point near in the near vicinity of a positive central charge because of its atmosphere is dependent both on the main charge as well as the surroundings with an effective radius so we actually derived this expression that the total potential is I.

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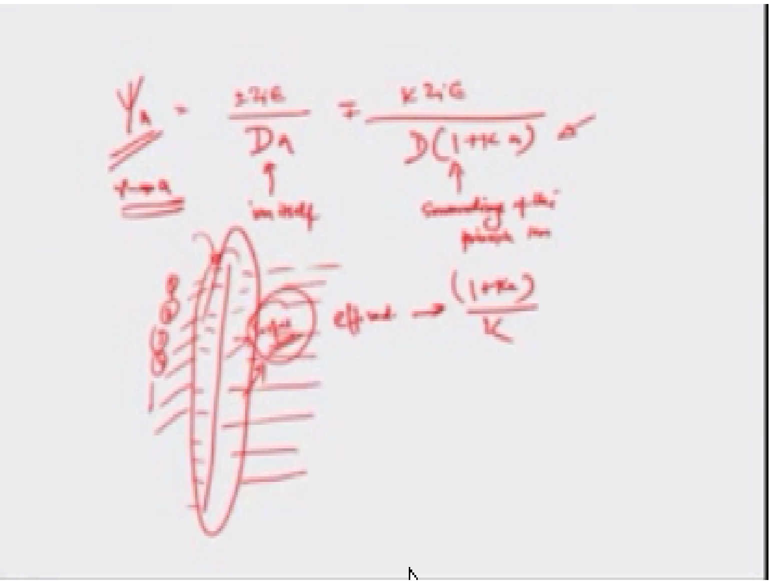

And could be recorded as + _ Z I epsilon D times of a which is actually due to the eye on itself and a contribution from the environment which is _ + k Z epsilon / by D 1 + K a where this contribution comes from the surroundings of the principal ion of the principal ion so we kind of found out that the effective radius that would bet here of the environment would be actually one by ka / by K.

So this was corresponding to the surface of the central ion of interest the ion was having a radius of a as you may recall and we had computed this expression with help of a charge equivalence saying that because you know of the electron neutrality principle the central ions charge would be same exactly same an opposite in nature to the total charge of the surrounding of the main Ion.

So having said that now let us look at the application of this to creating an array of such charges may be let us say there are negative charges which you know you want to create an array and that took on a surface so this is a surface of interest and we find out what are the effective processes which go on when there is a charge buildup of this one ion and surrounding translated into an embedded array of ions okay so these are all one-two three four there are several such negative ions embedded onto the onto the platform of the electrode and in vicinity.

With the solution okay so there is some kind of electrolyte and vicinity with that and you would like to compute what happens at this interface of the solid and the liquid so immediately when such a distribution happens for thecae of an electrode dipping into absolution of an electrolyte.

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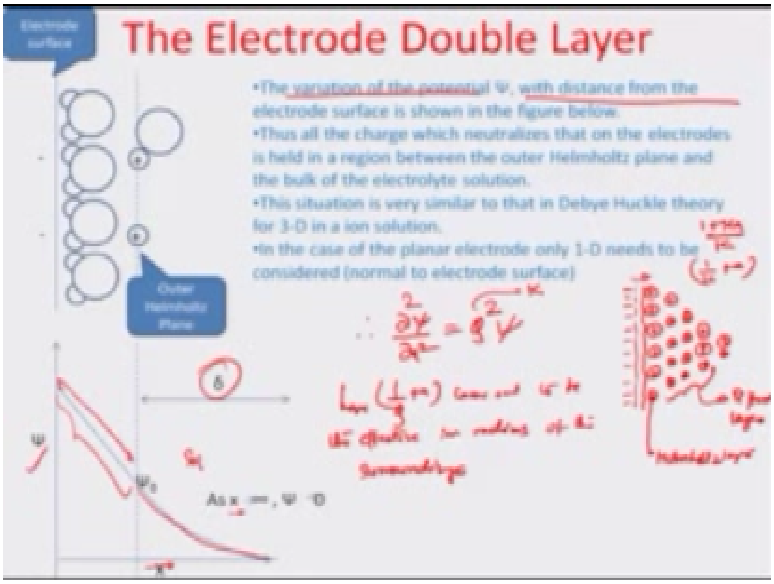

The Electrode Double Layer

- The variation of the potential Ψ, with distance from the electrode surface is shown in the figure below.
- Thus all the charge which neutralizes that on the electrodes is held in a region between the outer Helmholtz plane and the bulk of the electrolyte solution.
- This situation is very similar to that in Debye Huckle theory for 3-D in a ion solution.
- In the case of the planar electrode only 1-D needs to be considered (normal to electrode surface)

The total charge on the electrode surface must balance the total solution charged opposite charge because obviously if there are negative species on the surface it will attract all the positive ions from the solution and there is a thin layer of water this is a water layer maybe a mono layer of water which comes in between as a dielectric layer disabling the positive charge to go and settle on the top of this electrode as long as there is no active potential which is applied on this electrode.

So there is an electrostatic interaction between the electrode charge and the solution charged please be aware again that this charge is bound so it cannot really go into the into the solution unless there is a species which leaves with an excess electron or a four electron deficient deficiency into the into the solution so therefore it is always a bound to charge that we are talking about which is interacting with free charge which is like ions in the in the solution.

So this is the bound side okay of the child is you cannot have electron directly getting into the solution from the solid and that is because the electron is heavily bound by the nucleus of the different nuclei of the species which constitute the solid material so ions from the solution may approach the electrode surface only so far as their inner salvation shell sallow them to be so there is this is that shell that we were talking about the salvation cell shell because of which there is always you know mono layer of sort of water a membrane of water which comes between the iron and the even negative charge on the electrode and the surface array of ions is thus cushioned.

From the electrode surface by a mono layer of solvent the line drawn through the center of such ions at this distance of closest approach marks a boundary which is an imaginary boundary and we commonly know of it as an outer Helmholtz plane or a Helmholtz layer okay so this is the Helmholtz layer on the size of the ions forming the outer Helmholtz plane are larger

Than the total number of ions needed to do a complete charge balance obviously because these are very finely bound electrons which are densely present over the surface and this layer of negative charge really cannot be balanced because of a size constraint because every ion in the solution carries a size around it you have to mind.

That this is an eye on okay so this is having a specified size so this layer of charge which is the closest layer of charge that can come to the electrode is unable to balance the total charge which is on the electrode okay so therefore you have in the remaining charges which are all held within the with increasing disorder in the outward direction into the solution and this layer is known as a diffused part of the double layer.

So it is something like you have a densely populated negatively charged surface sort of a mono layer of salvation by water and then finitely a interest past charges of opposite type pulled by the electrode and then whatever remaining charge distribution or whatever remaining unbalanced charges are leftover there are several such layers which get formulated into the solution unless the charge balance is complete okay so obviously this is the Helmholtz layer.

And this whole layer of charge until the balance is complete is called the diffused layer so we are more interested in the variation of the potential say with distance from the electrode surface and if we were to plot this I can see somewhat characteristic value of Savoring as a function of x where x is the protruding distance into the solution the first layer up to the Helmholtz plane is really only resistive layer beyond which there is a square distance square influence.

Because of which you know the layer is no longer linear okay there is a charge unbalanced and that is how the charge assembles so this is the solution side but Taylor until the first layer of charges gets built up or the Helmholtz plane gets built up you have almost a resistive drop which happens only because of water okay and so let us assume that the diffuse layer extends all the way up to and we can try to calculate this from the presumptions made earlier.

If you may remember we had solved an equation of the type del 2 say I is the potential in the near vicinity of a charge by Del X 2 and this particular case on d1 Dimension X needs to be followed as it is a case of symmetry and also you know it is only a plane that we are referring to so it is not a three-dimensional space so we would only consider variation of the potential function with respect to the X here so this can be written down as q square zaiQ square is the equivalent of the capital K that we had done earlier in the case of single charge okay.

And here the 1 by Q + k if you may remember we had called this as 1 by ka / by K that is 1 by K + a as the effective Ion radius okay so this came out be the effective I on radius of the surroundings.

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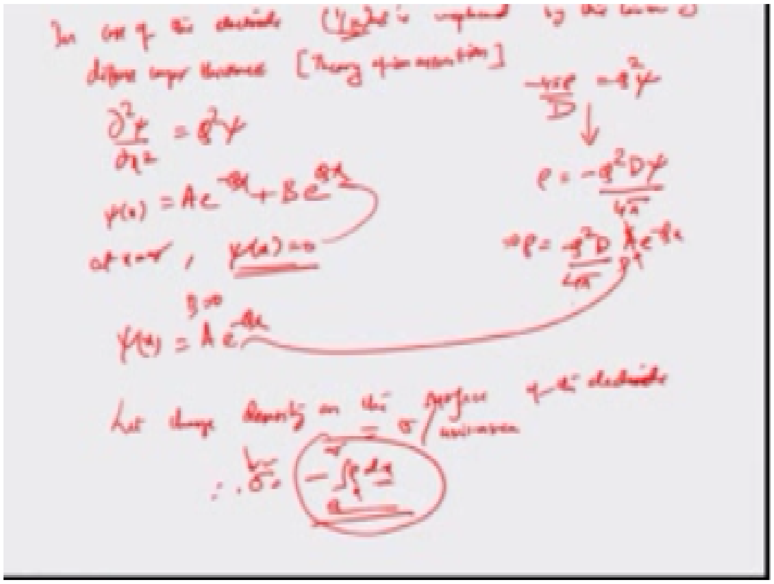

So having said that now in case of the electrode 1 by K can be replaced and this is only an approximation by the term which is the diffused layer thickness okay so this actually comes from the theory onion association and I am not going to go into the details of how this approximation came but you can just if any of you are interested interact you know on the chat portal further for you to be in able to learn a little more about this.

So this 1 by K can be approximated as the diffuse layer thickness in this particular case and obviously as you may recall this for gyro by D the _ sign is represented as q square is I in this particular case so we have general solutions of this equation del to Z by Del X 2 equal to Q squares I as z x equals a to the power of _ QX + B to the power of QX and at a distance X equal to infinity the say of X equal to 0 you can see here that corresponding to the infinite distance the potential kind of asymptotically goes all the way to 0 as one boundary.

From which we will be able to sort of predict maybe a few facts about this equation so obviously this is possible only when b is 0 the same manner and zee x in this key is the potential function is actually given by a to the power of _ QX okay and we already know from here that throw can be represented as _ Q is I by 4 in other words the row in this case the charge density can be_ q square d x 4 times of this value right here e to the power of _QX okay.

So in a similar manner we would like to try and see if we can calculate the value of a in this particular case and try to predict what is the potential function which is available at the at the almost you know Helmholtz layer surface and what is it as a function as it proceeds from the L molds layer all the way up to the end of diffuse layer so this is a very important perspective because art ultimately all the electrolysis that is going to happen is across this surface okay.

And this interface is a very critical you know issue when whenever we are talking about a solution in contact with a solid and on the solid side we have embedded electrons and on the liquid side you have ions. So that is the only way to sort of explain what is going on as interaction between the ions and the electrons available so here let charge density on the surface of the electrode we recorded a per unit area so obviously the value becomes equal to _ a to infinity ro DX okay or in other words this is what the surface charge density would be given the volume charge density okay.

Because we are only considering the difference in the X direction or the difference of the potential on towards the X direction so if I were to compute this integral I should be able to from the surface charge density or some other parameters able to kind of find out what is the value of a ok so let us actually do that here.

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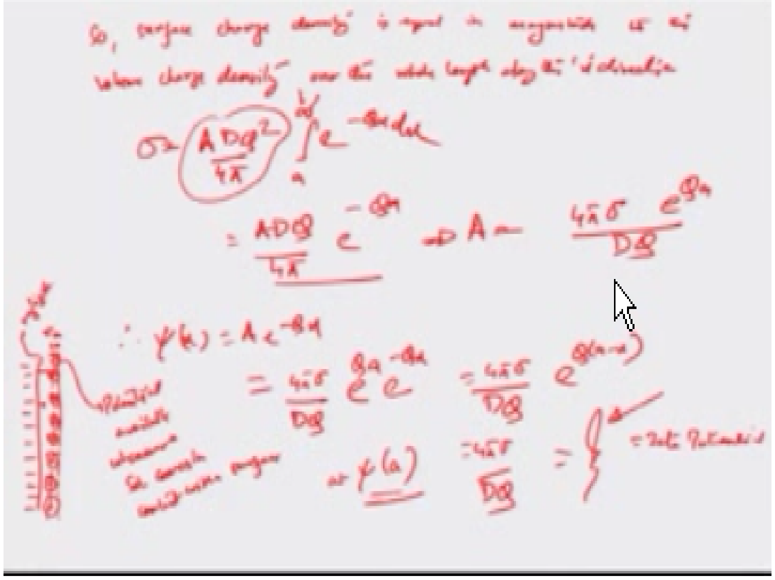

So, surface charge density is equal in magnitude to the volume charge density over the whole length along the 'x' direction

$$\sigma = \boxed{\frac{ADq^2}{4\pi}} \int_a^\infty e^{-qx} dx$$

$$= \underline{\frac{ADq}{4\pi} e^{-qa}} \Rightarrow A = \frac{4\pi\sigma}{Dq} e^{qa}$$

$$\therefore \psi(x) = A e^{-qx}$$

$$= \frac{4\pi\sigma}{Dq} e^{qa} e^{-qx} = \frac{4\pi\sigma}{Dq} e^{q(a-x)}$$

$$\text{at } \underline{\psi(a)} = \frac{4\pi\sigma}{Dq} = \zeta \leftarrow \text{Zeta Potential}$$

So the surface charge density is equal in magnitude to the volume charge density over the whole length along the X direction other words becomes equal to ad Q square by 4pi times of a to infinity e to the power of _ QX TX I have substituted the value of Rho here to calculate this expression and this comes out to be equal to ad Q / by 4 e to the power of _ Q a because obviously one of the limits is X equal to infinity.

So this is how surface charge density is related and in other words I can always say that the value of a which is the unknown constant in the differential equation comes out to be 4 e to the power of q a / by DQ and in other words if were to substitute this back into the expression roe x which is actually AE to the power of _ QX would have four by DQ e to the power of Q a _or times of e to the power of _ Q X in other words for by DQ P to the power of QA _ X.

So if we just look back into what really the formulation was we have a solid side with a densely embedded negative charge on the surface we have a salvation layer which is in between and then there is a Helmholtz layer which gets formulated so if we assume the salvation layer to be very small in comparison to the you know the ionic radius and at the surface of the cell molds layer you have exactly X equal to a okay.

This value is considered to be negligible The Salvation cell shell any event it is only a one layer of water so we get this value here as for d q s y at a times e the power of 1 so this actually is the potential available whenever a solution comes in contact with a surface and we call this potential normally the zeta potential so this is a very important term as regards electrochemistry because it is the zeta potential which is going to be able to actually define some of the things that we do in electrochemistry.

So there are there are again you know if we really looked at effectively two components which make up the total potential drop across the interface obviously there is a potential drop which is in this particular Helmholtz layer and then there is a drop which is there in the diffused layer so if we looked at this model as a capacitance model we would definitely have the total capacitance of the double layer C made-up of that due to the inner layer and which we designate as let us say the molds layers eh and that due to the diffuse layer which may designate again as CD.

So we can have this total capacitance here all the way up to let us say the diffuse layer here as see a combination you know a series combination of CH and CD okay so we can have 1 by c equals 1 by c h + 1 by so that the total net capacitance comes out to be c at CD by ch+ CDN there are two different cases if supposing the CD value is much less in comparison to CH then the effective capacitance let us say s this is C effective becomes equal to CD okay and if CD is very high in comparison to CH the effective capacitance becomes equal to CH so this is called the Helmholtz model.

Where reconsider Helmholtz capacitance to be negligible and this actually is known as the guy chap and model and this are important for the perspective of doing electrochemistry at a surface whenever we want to take care of the measurementshowever we are more interested in the zeta potential and the way that the electrochemistry may happen on an ECMprocess okay and for that now let us actually go back into the very fundamental basics about our mass transport occurs and what is the electron exchange process considering a ECM operation.

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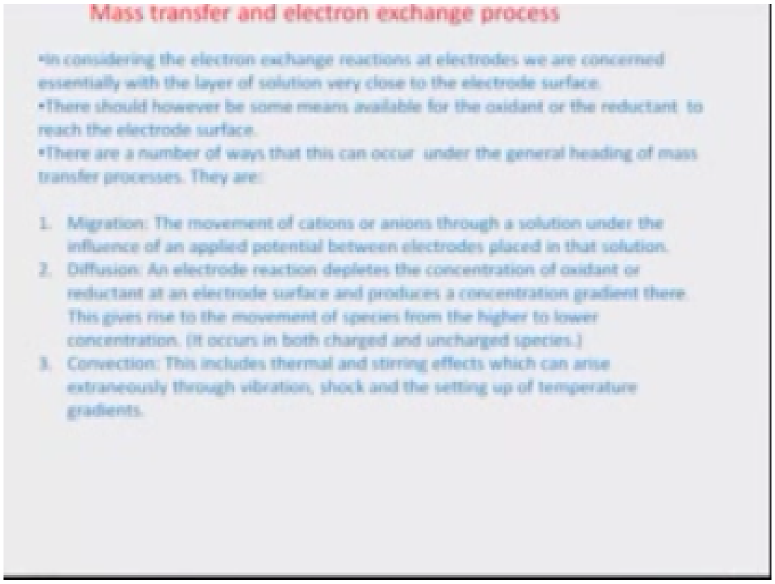

Mass transfer and electron exchange process

- In considering the electron exchange reactions at electrodes we are concerned essentially with the layer of solution very close to the electrode surface.
- There should however be some means available for the oxidant or the reductant to reach the electrode surface.
- There are a number of ways that this can occur under the general heading of mass transfer processes. They are:

1. Migration: The movement of cations or anions through a solution under the influence of an applied potential between electrodes placed in that solution.
2. Diffusion: An electrode reaction depletes the concentration of oxidant or reductant at an electrode surface and produces a concentration gradient there. This gives rise to the movement of species from the higher to lower concentration. (It occurs in both charged and uncharged species.)
3. Convection: This includes thermal and stirring effects which can arise extraneously through vibration, shock and the setting up of temperature gradients.

So in considering such electron exchange reaction at electrodes we are concerned essentially with the layer of solution very close to the electrode surface there should however be some me is available for oxidant or the reluctant to reach the electrode surface and the number of ways which this can occur under general heading of mass transfer processes and they are migration is a movement of captions orations through a solution.

Under the influence of an external potential between the electrodes placed in that solution diffusion is basically concentration gradient driven flow the electrode reaction depletes the concentration of the oxidant or reluctant add the electrode surface and produces a concentration gradient there.

So this gives rise to the moment of species from the higher to the lower concentration it occurs in both charged and uncharged species and then we have convection which is because of again the thermal or the stirring effects which can arise extraneous Lee through vibration shock setting up of temperature gradients within the electrolyte so these are the three mainmasts transport mechanisms which would influence the traveling of the ion across the salvation shell.

So that there is you know deposition on the electrode of one kind and similarly taking out of the solid from the electrode of at the other electrode or the other potential arise so generally in the ECM electrochemistry.

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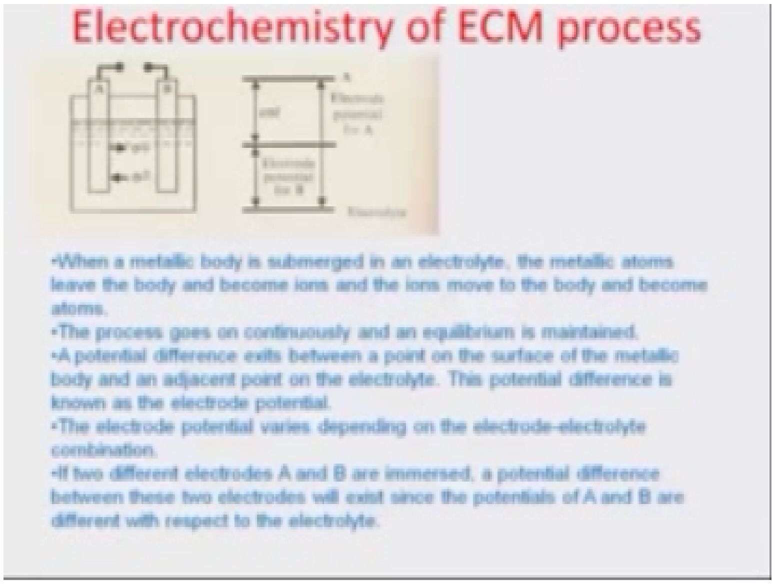

Electrochemistry of ECM process

•When a metallic body is submerged in an electrolyte, the metallic atoms leave the body and become ions and the ions move to the body and become atoms.
•The process goes on continuously and an equilibrium is maintained.
•A potential difference exits between a point on the surface of the metallic body and an adjacent point on the electrolyte. This potential difference is known as the electrode potential.
•The electrode potential varies depending on the electrode-electrolyte combination.
•If two different electrodes A and B are immersed, a potential difference between these two electrodes will exist since the potentials of A and B are different with respect to the electrolyte.

When a metallic body is submerged in an electrolyte the metallic atoms leave the body and become ions and the ions move to the body and become atoms okay so the process goes on continuously and an equilibrium is maintained and the potential difference exists between appoint on the surface of the metallic body and an adjacent point on the electrolyte and this potential difference is known as the electrode potential which is also the zeta potential and the electrode potential varies depending on the electrode electrolyte combination and if two different electrodes a and B are amassed potential difference between these two electrodes.

Will exist since the potentials of a and B are different with respect to the electrolyte which may result in some kind of a current or a you know voltage difference between both the electrodes a and B so this is the general electrochemistry process and how the ECM can be obtained from this electrochemistry process is the following manner.

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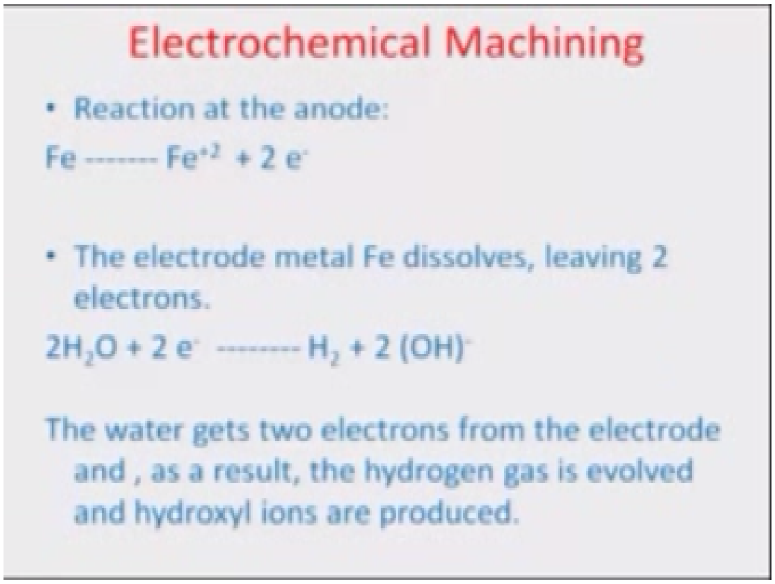

Electrochemical Machining

- Reaction at the anode:

Fe ------- Fe^{+2} + 2 e^-

- The electrode metal Fe dissolves, leaving 2 electrons.

$2H_2O + 2e^-$ -------- $H_2 + 2(OH)^-$

The water gets two electrons from the electrode and , as a result, the hydrogen gas is evolved and hydroxyl ions are produced.

So let us say hey there action at an anode is basically related to steal so we having the faith you know the iron two ferrous ions conversion process meaning thereby whatever iron is there on the surface leaves as f e + two ions on the solution and leaves two electrons with the electrode concern okay now if supposing we had the brine solution or just normal kitchen salt water combination the electrode metal Fe would dissolve okay and the two electrons that have been left because of that would actually further try to break down water into h2 which is a gas form and it kind of bubbles out and hydroxyl ions 20 h_ okay .

Now you can think of it that there is f e 2 + present in the solution because of the removal from the electrode and then there is this two electrons which are depleting the hydrogen ox I mean the water into the hydrogen gas and hydroxide ion so obviously there would be a reaction between this oh h and the f e + two because of its availability in abundance within the within the medium and as a result you can have Ferris hydroxide foe h 2 formulated in the medium.

Which is actually a precipitate okay so it is an insoluble form of compound of iron and it precipitates and it actually is there you know at the bottom of the electrochemical beaker or the jar where this whole reaction is taking place now so this is something very interesting happening that on one hand you are able to do you know the reverse of electroplating by taking out iron from one of the electrodes converting it into the ionic state.

And then using the same electrons at iron had given earlier to convert this f e + 2 into feo h2 hydroxide which is actually insoluble ok so it does not redeposit on the other electrode through which the electron has been pumped in and at the same time it goes and falls at the bottom okay so whatever is coming out is not getting deposited in the other electrode in other words it is going to be subtractive process or machining is happening.

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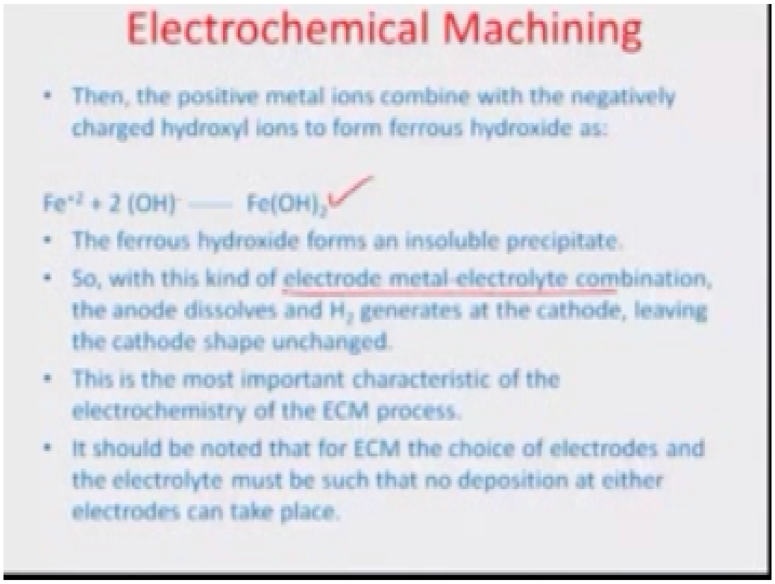

Electrochemical Machining

- Then, the positive metal ions combine with the negatively charged hydroxyl ions to form ferrous hydroxide as:

$Fe^{+2} + 2\,(OH)^{-} \text{ —— } Fe(OH)_2$ ✓

- The ferrous hydroxide forms an insoluble precipitate.
- So, with this kind of electrode metal-electrolyte combination, the anode dissolves and H_2 generates at the cathode, leaving the cathode shape unchanged.
- This is the most important characteristic of the electrochemistry of the ECM process.
- It should be noted that for ECM the choice of electrodes and the electrolyte must be such that no deposition at either electrodes can take place.

You know at the behest of this reaction so with this kind of electrode metal electrolyte combination the anode dissolves and hydrogen generates at the cathode leaving the cathode shape unchanged and this is the most important characteristics of ECM process that when we are doing a dye syncing process with DCM I had mentioned it earlier the shape of the cathode which is actually the tool in our case and is also an electron emitter does not change so whatever is the dye or whatever is the overall shape of the cathode remains as such and it is useful amending forum bidding on to the surface.

Which is being machined so it should be noted that for ECM the choice of electrodes and the electrolyte must be such that no deposit in and either electrodes can take place of whatever is coming off and that's how electrochemical machining is sort of perform so let us now look at the little bit of you know how you calculate the material removal rate and I think I had earlier illustrated the Faraday's law through which we had you know the mass that is taken off or transported in a electrochemical system.

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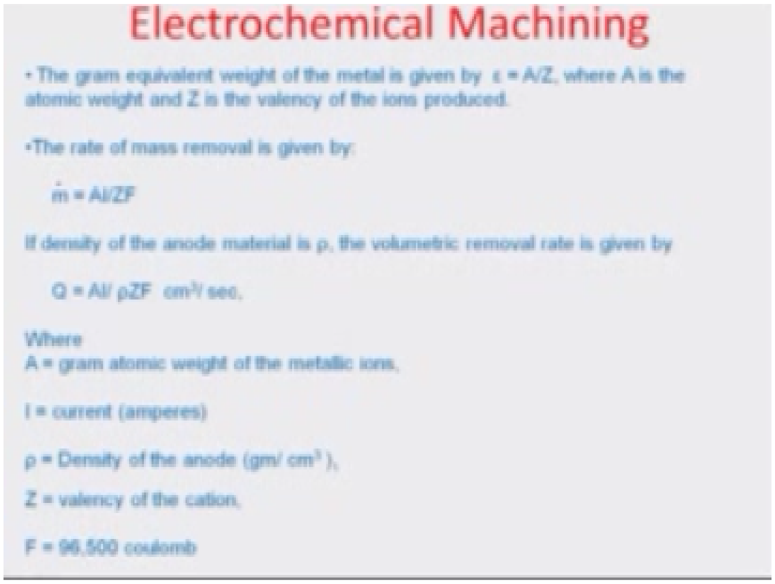

Electrochemical Machining

- The gram equivalent weight of the metal is given by $\varepsilon = A/Z$, where A is the atomic weight and Z is the valency of the ions produced.

- The rate of mass removal is given by:

$$\dot{m} = AI/ZF$$

If density of the anode material is ρ, the volumetric removal rate is given by

$$Q = AI/\rho ZF \ \ cm^3/sec.$$

Where

A = gram atomic weight of the metallic ions,

I = current (amperes)

ρ = Density of the anode (gm/cm^3),

Z = valency of the cation,

F = 96,500 coulomb

And it is dependent on the current time product and is also related to the gram equivalent weight of the species so for borrowing this theory we can probably try to see what is the most okay so that the material removal rate the rate of mass removal and we can call this by putting a very interesting you know term here which is this faraday constant and we assume this movement of material as moles okay.

And you know that one mole is 6.0 2 3 into 10 to the power of 23 atoms or species or ions or whatever it gets dissolved so basically we are considering only the molar mass and all you know things related to amole or number of moles being transferred which makes it easy because as you know that the weight of one mole of the species exactly equal to its atomic weight okay so that is how in chemistry in basic fundamental chemistry.

Things have been categorized so here also a similar manner the m dot or the rate of removal of the mass obviously depends on the I the current which is the rate at which charge is transported so basically do not have the current time product anymore but the MDOT enables this current time product to change on Lee into current times of the gram equivalent weight which is again function of the atomic weight that is the movement of you know or that is the mass of one mole atom of particular species the valiancy which is needed obviously if you are removing + two you have to have two electron transfer.

So number of charges that would be needed for removing Fe+ two would be exactly two times or two moles you know for one mole of Fe+ two so that ratio needs to be maintained here which is actually given by this a by Z or equivalent weight and this is also related to sort of you know this I is still charge and we need to somehow change into you know from the rate of transport of charge into rate of transport of moles of charge.

So we divide this by the charge of one mole electrons and one mole of electrons would have 6.02 3 10 to the power of 23times of 1.6 10 to the power of _ 19which is the charge on one electron Coolum and this figure comes out to be90 6500 Coulomb approximately okay so that is how faraday constant F is derived so if want to multiply this or divide this I which is the DQ by DT or the rate of change of odd rate of transfer of charge into the solution of into the electrochemical set up by this term F it would typically mean.

What is the rate at of what is the rate of molar change of charge within the species so it would be very good way because in one mole you know that a by Z mass is removed ok so the m do therefore which is also the material removal rate in grams per second ok is given by AI by ZF if i were to convert this into the volume rate of removal of material I would have to divide this by density Rho and so effectively the material removal rate in centimeter cube per second comes out to be and this is the volumetric material removal rate comes out.

And it to be a I by Centimeter cube per second AO is the atomic weight Graham atomic weight of the metallic species the I is the current in amperes Rose the density of the anode in gram per centimeter cube and Z obviously is the valiancy of theca ion and I've already explained to you how this F factor or the faraday constant is emerged so this is the sort of ballpark understanding of how the volumetric material removal rate can be created however this is only a single-phase.

System but in actual real scale operations you do phased alloys and therefore each of the alloys or each of the elements participating in those alloys are having a different characteristic density different characteristic weight so we will try to in simple or envision model where all these allow its systems are present and how do we do the rate calculation in that case would be the next step that will like to do but I have to close this module in the interest of time so as of now goodbye from here next module we are going to do allow it systems thank you.

Acknowledgement

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