Microsystem Fabrication with Advanced Manufacturing Techniques

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Lecture – 12

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Microsystems Fabrication by Advanced Manufacturing Processes-Lecture 12

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Hello and well come back to this lecture 12 on Microsystem Fabrication by Advanced Manufacturing Processes like to briefly recap what I talked last lecture.

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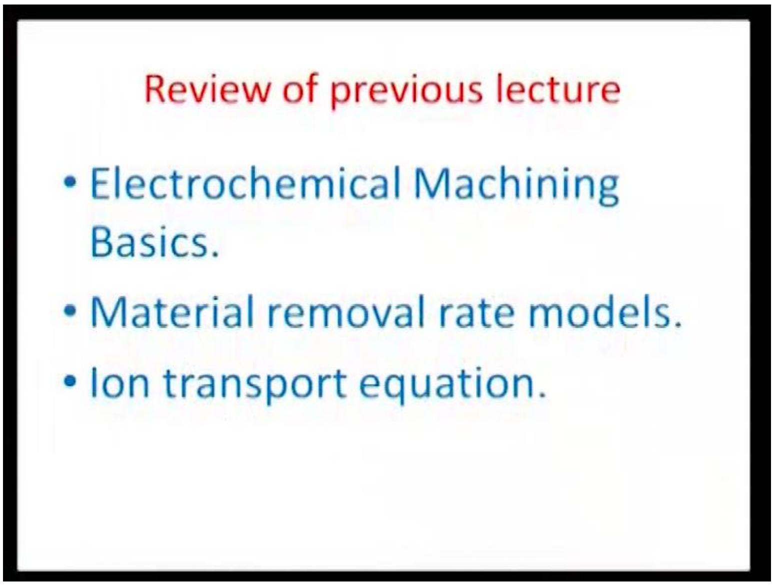

Review of previous lecture

- Electrochemical Machining Basics.
- Material removal rate models.
- Ion transport equation.

So, we are talking about Electrochemical machining some basics and fundamentals I would like to just mention here that it is process where the tool is made the electron the cathode the work pieces made the anode. And then the choice of electro light is d1 in a manner. So, that what about dissolve of the anode those are the precipitate into the solution and then it circulated. So that there is no deposition back on the tool cathode and this way, the whole processes used or is made I mean able to machining of materials.

So, we also did some estimation of material removal rate and we studied paradise law in the process and we were at to sort of predict, what amount of in a material per any time may be removed by this process. When we started looking at the very first important thing in electro chemistry in many electro chemical operation, which is the iron transfer equation ok.

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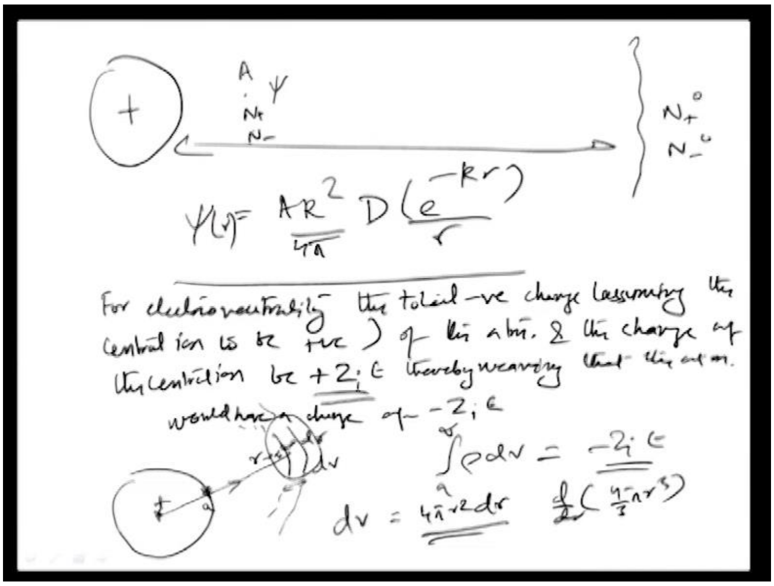

$$\psi(r) = \frac{AR^2}{4\pi} D\left(\frac{e^{-kr}}{r}\right)$$

For electroneutrality the total −ve charge (assuming the central ion to be +ve) of the atm. & the charge of the central ion be $+Z_i e$ thereby meaning that the atm. would have a charge of $-Z_i e$

$$\int_a^\infty \rho\, dv = -Z_i e$$

$$dv = 4\pi r^2 dr \quad \frac{d}{dr}\left(\frac{4}{3}\pi r^3\right)$$

So, as a part of that equation you may remember we had actually is try to study what the impact of positive ion of interest would be an assembling it is negative charge atmosphere around it. And we studied that, what the potential would be had a function at a point a, if you assume that there is a charge number of density represented by n plus 0 and n minus 0 and near this a it is n plus and n minus.

So, we try to find out the potential arising out of the situation in the psi was represented as a square of k by 4 pi directed constant d times of e to the power of minus k r by r. So, that is how psi potential at point a would be function of r. So, for the electro neutrality the total negative charge assuming the central ion to be positive of the atmosphere about a given ions of the atmosphere and the charge of the central ion be plus z i epsilon they are by, that the atmosphere would have a charge of minus zi E.

So, we can assume that let say if you have the central ion here and you are looking at some distance r from this ion, as if there is a shell of thickness d r around this distance r and then, you say that there is a distance a or the parameter. At which, the you know the ion kind of just truncated, so this is the radius of the ion. So we can assume, that the total charge which is available, because of this positive central ion of the interest can be represented as the value dv here times of the value in charge density at this point.

So, row times of dv right and this varies between let say some distance a all the where 2 1r goes to infinity. And that can be made equivalent to the charge minus zi E the total charge in the atmosphere around the central ion of interest. So dv of course, as you know is nothing but 4 pi r square d r is d y d r of sort of 4 by 3 pi r q. So, that is how the value element of the shell a would be around this whole central charge of you know interest.

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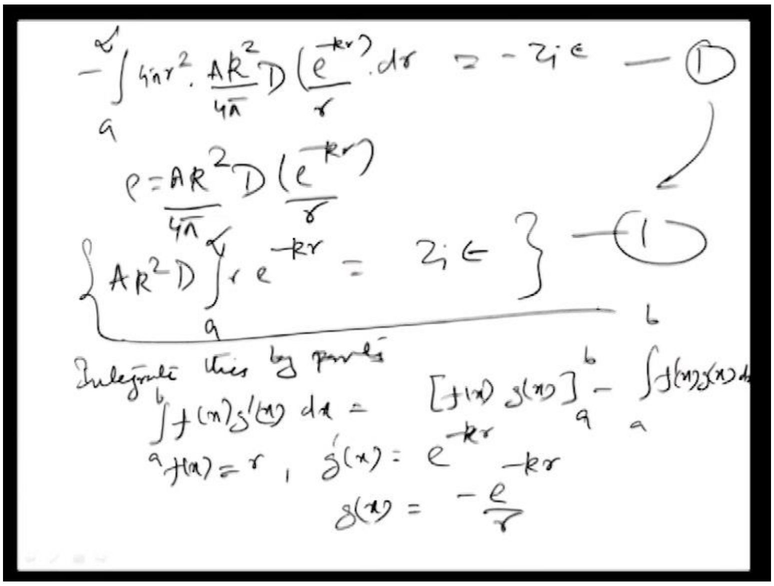

$$-\int_a^\infty 4\pi r^2 \cdot \frac{AK^2}{4\pi} D \left(\frac{e^{-kr}}{r}\right) . dr = -z_i \epsilon \quad — ①$$

$$\rho = \frac{AK^2}{4\pi} D \left(\frac{e^{-kr}}{r}\right)$$

$$\left\{ AK^2 D \int_a^\infty r e^{-kr} = z_i \epsilon \right\} — (1)$$

Integrate this by parts

$$\int_a^b f(x) g'(x)\, dx = \left[f(x)\, g(x)\right]_a^b - \int_a^b f(x) g(x)\, d$$

$$f(x) = r, \quad g'(x) = e^{-kr}$$

$$g(x) = -\frac{e^{-kr}}{r}$$

And therefore,, the value integral a to infinity of 4 pi r square times of row charge density which has been represented earlier you know that row has been represented earlier has Ak k Ak square by 4 pi d into the power of minus kr by r. So, this charge here a times r square of k by 4 pi D times of e to the power of minus kr by r times of dr. So, that is equal to minus zi epsilon, and therefore we can just simplify this equation let this equation 1.

So, we can simplify this equation further 2 often A square of kD by times of integral 0 to a 4 or r times to the e to the power of minus kr equals to zi E. So, because there is a minus terms which is comes from the potential the charge density. So, that is the final integral that we have to solve. So, we have to integrate this expression by parts as you know that we know that formula was integration by parts as a 2 b f x g dash x dx equals fx gx between the same limits minus integral a to b of f dash x times of gx times of dx. And here as you know that, fx equal to r and gx or g dash x if we assume, it does it e far of minus kr there why meaning that gx can be equal to minus e to the power of minus kr by r.

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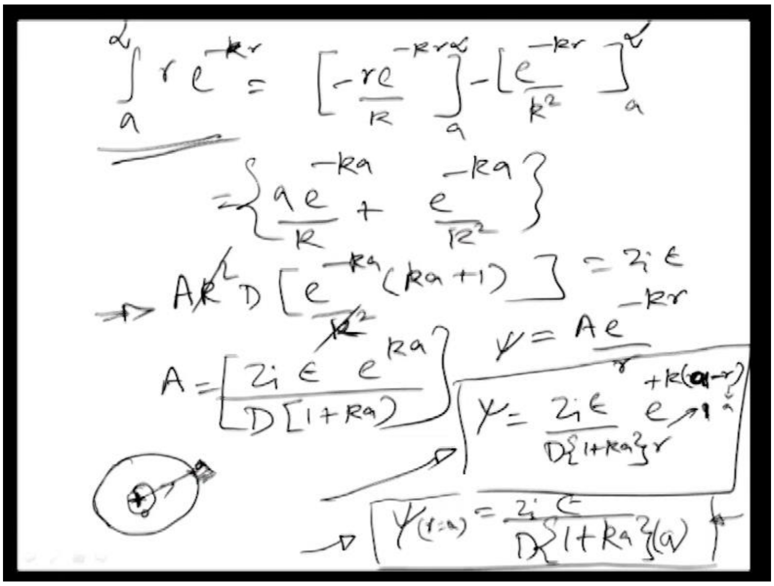

$$\int_a^{\infty} r e^{-kr} = \left[-\frac{r e^{-kr}}{k}\right]_a^{\infty} - \left[\frac{e^{-kr}}{k^2}\right]_a^{\infty}$$

$$= \left\{\frac{a e^{-ka}}{k} + \frac{e^{-ka}}{k^2}\right\}$$

$$\rightarrow A \cancel{k}^2 D \left[\frac{e^{-ka}(ka+1)}{\cancel{k^2}}\right] = z_i \epsilon$$

$$A = \left[\frac{z_i \epsilon \, e^{ka}}{D[1+ka]}\right] \qquad \psi = \frac{A e^{-kr}}{r}$$

$$\boxed{\psi = \frac{z_i \epsilon}{D\{1+ka\} r} e^{+k(a-r)}}$$

$$\rightarrow \boxed{\psi_{(r=a)} = \frac{z_i \epsilon}{D\{1+ka\}(a)}}$$

So we can actually, write this whole expression on by parts as integral a to infinity re to the power of minus kr as minus r e to the power of minus kr by K varying between a and infinity minus of e to the power of minus kr by square of k varying between a. And infinity and this therefore, can be further represented as ae to the power of minus K a by k plus e to the power of minus k a by square of k and simultaneously we can have A square of k times of D times of e to the power of minus k a by k, because edges substituting this result into the equation formulated earlier here. The equation 1 right, it has been just the same equation formulated earlier. So therefore, into the power minus k by k times of square of k times of ka plus 1 equals zi e. or in other words, as you already know that on the potential function psi is A to the power of minus kr by r and a from here can be found out has square of k those away. So, we are left with zi epsilon divided by D times of 1 plus ka e to the power of ka as A.

And potential function psi can be represented as zi epsilon D to the power of a D times of 1 plus ka times of r times of e to the power of minus k or less plus k a minus r. So, that is how the potential function psi can be calculated as.. So, I would like to now just sort of bring you know your attention to what would happen at the surface of the charge central ion, which is at a distance a from the center of the ion.

So, we can assume that this influence or domain of the charge varies between r equal to 0 and a although the charge is kind of super concentrated at the center of the ion. So, that is the concept of a point charge and charge is concentrated at the point but, then it can have a radios 0 to a. So, at a the potential because of the charge which is somewhere here of hidden here can be represented as psi at r equal to a is zi epsilon by D times of 1 plus ka times of a r equal to a and when you put r equal to a here this exponential term goes away. So, this equal to 1.

So therefore, that is how the potential at point a on the surface of this point charge can be recorded as. We can further, try to sort of split this into a partial fraction and try to have look into what all components would go and formulating potential at the point a.

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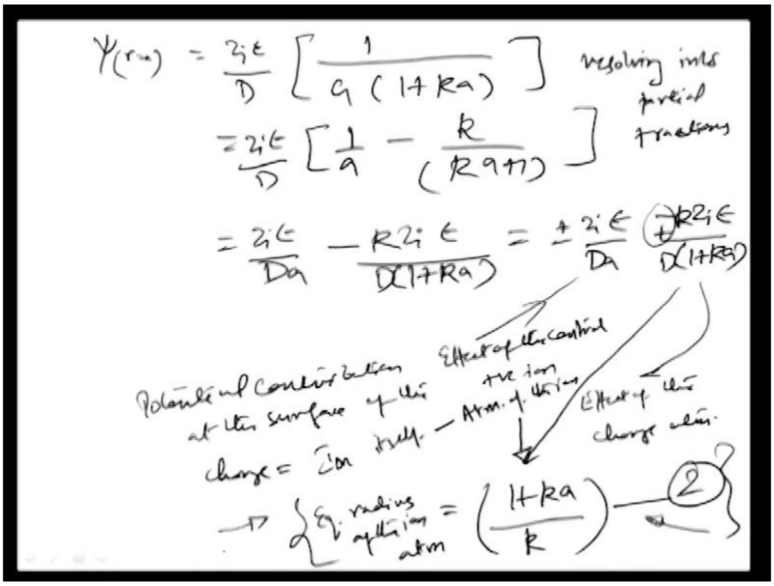

$$\psi_{(r=a)} = \frac{z_i\epsilon}{D}\left[\frac{1}{a(1+ka)}\right]$$ resolving into partial fractions

$$= \frac{z_i\epsilon}{D}\left[\frac{1}{a} - \frac{k}{(ka+1)}\right]$$

$$= \frac{z_i\epsilon}{Da} - \frac{kz_i\epsilon}{D(1+ka)} = \pm\frac{z_i\epsilon}{Da} \mp \frac{kz_i\epsilon}{D(1+ka)}$$

Potential contribution at the surface of the charge = Ion itself — Atm. of the ion

Effect of the central +ve ion

Effect of the charge atm.

$$\rightarrow \left\{ \text{Eq. radius of the ion atm} = \left(\frac{1+ka}{k}\right) \right\} \text{②}$$

So here let say, this psi therefore at r equal to a can be written down as zi E by d times of 1 divided by a times of 1 plus k a meaning there by it can be zi E by d times of 1 by a minus k by ka plus 1 this is how would happen when it is resolved into partial fractions. And we can represent this z i E by da minus k times of z i E by d times of 1 plus k a and this can further be expressed x plus minus zi epsilon by Da minus plus depending on the value of charge k zi epsilon by D times of 1 plus ka.

So, just for the by the look of it at p this can be the effect of the central positive ion and this components because, it is exactly the opposite of it can be the effect of the charge atmosphere which is principally negative charge. So therefore, you know the potential contribution at the surface of the charge would come due to the ion itself and due to the atmosphere of the ion and the equivalent radius of this ion atmosphere can be treated to be 1 plus ka by k.

So, this is the from this term here this is the equivalent radius of the ion atmosphere. And this let this be called equation 2 here and this would be some relevance because, we will try to utilize this not at to find out, what is the potential of such a surface which would get which is nothing, but an on assemblage of the charges of 1 time with respect to the charges of other type which is represent lined up as the hemisphere near the surface z will layer.

So, design atmosphere would become very relevant in calculating the potential of the surface at that stage. But you do understand that, the contribution of the ion atmosphere on to the ion's surface also is of equal amount of significance and relevance in this particular illustration.

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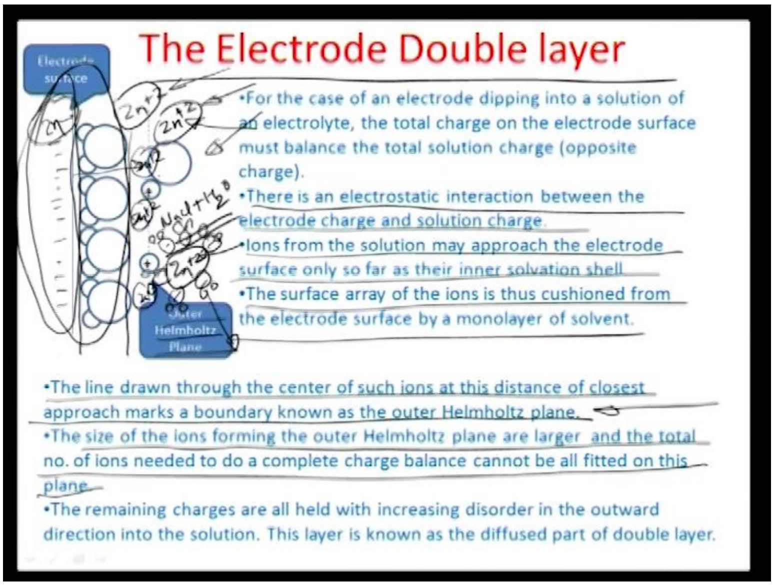

The Electrode Double layer

- For the case of an electrode dipping into a solution of an electrolyte, the total charge on the electrode surface must balance the total solution charge (opposite charge).
- There is an electrostatic interaction between the electrode charge and solution charge.
- Ions from the solution may approach the electrode surface only so far as their inner solvation shell
- The surface array of the ions is thus cushioned from the electrode surface by a monolayer of solvent.
- The line drawn through the center of such ions at this distance of closest approach marks a boundary known as the outer Helmholtz plane.
- The size of the ions forming the outer Helmholtz plane are larger and the total no. of ions needed to do a complete charge balance cannot be all fitted on this plane
- The remaining charges are all held with increasing disorder in the outward direction into the solution. This layer is known as the diffused part of double layer.

So, let us now look at some of the very basic fundamentals of what happens when a electrode is dipped in a solution which creates an assembly of the charges cut. So, let us now look into slightly different aspect of the double layer as was mentioning before. So, how does the double layer get formulated, let say this is the electro surface that we are looking at and this Zinc and this is emerstin just a brine solution Na cl plus H2 O salt water.

So, there is an automatic tendency of the Zinc to formulate Zinc ions. So, they would actually Beyoncé of Zinc which would come out dissolved manner from the electrode. And there would be water molecules which would be immediately encircling Zinc. So, call so this is the water molecules encircling the Zinc and that is how this whole orientation would be… So, each of the Zinc atom is surrounded by of molecules and that is true for all these Zinc atoms which are there in the solution.

And correspondingly, there are negative ions which are there on the electrode surface. So, there are positive ion's in the solution and negative ion's in the electrode surface. So, they should be equal and opposite if there is no external field that is influencing the system because, whatever number of Zinc atoms are liberated assign into the solution should have charge wise the similar amount of electrons and the electrode surface.

So, what is important in worth he would mention is that there is a thin layer of water we should come between the positive charges and the ions separating them from each other. And there the Zinc plus 2 cannot get deposited back on to the electrons and this becomes electron reach and there is a feel which, exists between the you know the first layer of Zinc ions which are here and this is known as the Helmholtz layer, and the layer of electrons which are on this other side here.

So, there is an electrostatic interaction between the electrode charge and solution charge that is number 1 and then, ions from the solution may approach the electrode surface only so far as their inner salvation shell, so salvation shell is to this shell which is formulated because of the watermelon around this Zinc wrest datum. So, as much as this salvation shell can allow, only that much distance the ion can have in proximate to the electrode charge the electronic charge which is on the electrode.

So, the surface array of the ions is thus cushi1d from the electrode surface by a monolayer of solvent. In the line drawn through the central of such ions at this distance of closest approach marks a boundary and this is known as the outer Helmholtz plane. Thus indicated here this is the an of all the Zinc plus 2 atoms hold on to a certain line, on the size of the ions formulating the outer Helmholtz plane are larger and the total number of ions needed to do a complete charge balance cannot be all fitted on this plane.

So, obvious reasons that electron here and the electro is the part of the electronic structure much more decidedly fact in comparison to the ions which had in the solution which are positive plane and. So, therefore not 1 layer, but subsequently a set of layer would be needed.

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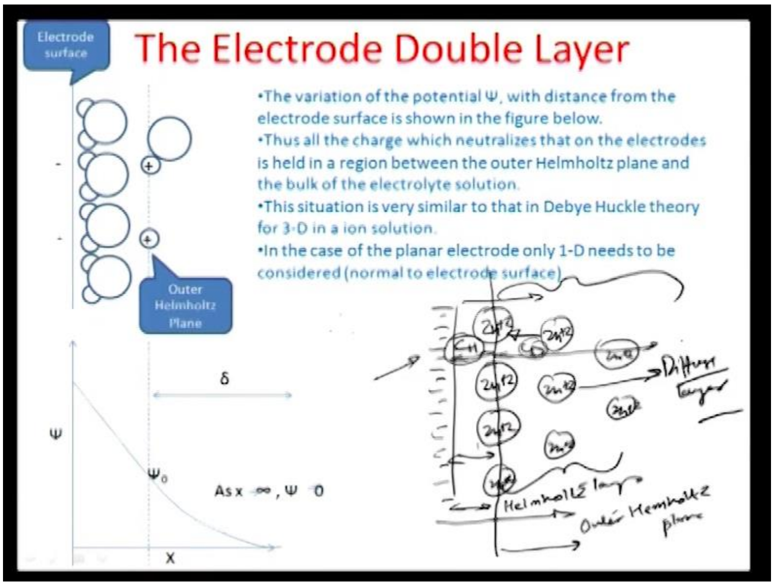

The Electrode Double Layer

- 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)

So for example, let us suppose this is the electrode surface and you have negative charge assemble here and to the electrode surface. So, the first set of Zn and plus 2 ions would not be able to take care of the total electronic charge which has been emanated in the surface this is mind you are… So, it is showed of automatically impregnated in to the surface these electrons are and these are full size hands and the solution.

There has to be subsequent layers which would be responsible for whatever field escapes is the first line of ions and then, slowly the feel gets neutralized and the ion layers get thinner and thinner as usually you go radially from the electrode in to the solution. So, typically this layer, in a such a case is known as the first layer of charge and so it is the Helmholtz layer and this is demarcated by this Outer Helmholtz plane.

And this layer here write here is short of diffuse layer of charges and therefore, in electro chemistry mostly there is a Helmholtz layer and then there is a diffused layer, which has its shown contribution in terms of capacitance. So, this is CH and this is CD. So, the capacitance of the Helmholtz layer is what generates because of this solvation shell of individual ions separating by ions from getting back in to the electrodes fact to the electrons and the diffuse layer which is there in formulated inside the solution.

So, that is what the orientation here is. So, therefore the remaining charge are all held as we know with increasing the order disorder in the outward direction in to the solution and this is known as the diffuse layer of the charges. So, that is why double layers, so you have a 1 layer which is the Helmholtz layer and then other layer which is a diffuse layer of the charges.

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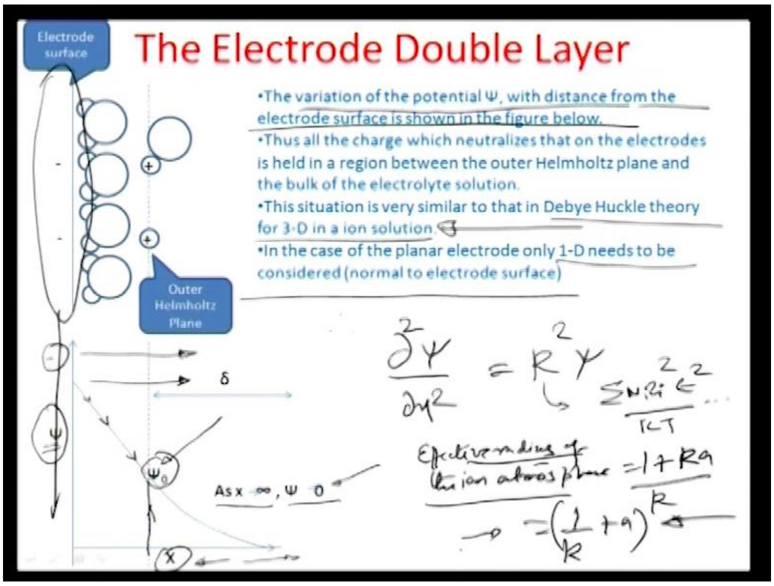

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As x ∞, Ψ 0

$$\frac{\partial^2 \Psi}{\partial y^2} = K^2 \Psi$$

$$\frac{\sum n_i z_i^2 e^2}{kT} \ldots$$

Effective radius of the ion across plane $= 1 + Ka$

$$= \left(\frac{1}{K} + a\right)^K$$

So, that is how in not shall the you know the hole electron is oriented with reference to the solution. So, let actually now looking to how the potential zeta would vary with respect to distance from the electrode surface. So, if you the in the potential zeta with respect to acts in cover distance in to the solution, as you can see the potential where is linearly like this solve the wave of thus value here which is the actually as will written on tell you the zeta potential of the surface.

Then, after that the moment crosses Outer Helmholtz plane the potential start the warring of the diffused layer in a it is not a it is non-linear behavior in this particular zone. So, we had to somehow we able to find out what does potential function is with respect to acts and as; obviously, as we have done before infinity the potential function a zeta is actually to equal to 0.

So, this calls for the solution of the Debye Huckel theory in 3 dimension as we did just about few slide back and in a ion solution to a 1 d case: a 1d is only the dimension of interest from the area of ions which are somewhere here on the electrode, so these the area ions. And with respect to that area of ions maybe we can considered these all focus to want to single place with respect to this 1 let us say, central ion as an available in format on the electrode, what is the distribution of the charge in the solution.

Thereby, in the potential function would be recalled in that case and if simply 1 dimensions approximation is the Foshan equation we can just write d2 psi by dull x2 is actually equal to square of k times of psi as you already no from a in linear equation this score of k is basically, the function which comes in a terms of sigma ni zi square over epsilon by the kt times up so on so forth.

So, that is what the case for term is here, also what is of interest and significant is that as we found out last time that with respect to the center line; the there is an effective radius of the ion atmosphere and this effect the radius was given by 1 plus ka by k in other words, it means because 1 by k plus a. So, that was the radius of the effective surrounding ion atmosphere with respect to the central charge of interest. So, we considered the similar value here and try to see what thus the function results.

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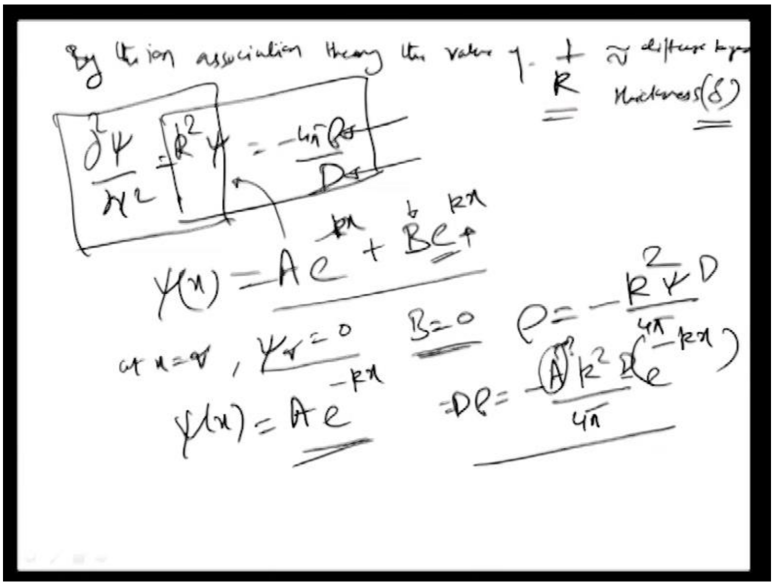

By the ion association theory the value $\frac{1}{k} \approx$ diffuse layer thickness (δ)

$$\frac{\partial^2\psi}{\partial x^2} - k^2\psi = -\frac{4\pi\rho}{D}$$

$$\psi(x) = Ae^{-kx} + Be^{kx}$$

at $x=\infty$, $\psi_\infty = 0$ $\quad B = 0$ $\quad \rho = -\frac{k^2\psi D}{4\pi}$

$$\psi(x) = Ae^{-kx} \qquad -D\rho = -\frac{A k^2 D(e^{-kx})}{4\pi}$$

So, by the theory of ion association I would just like to simply stated without really getting in to the proof of head. But by the ion association theory the value of 1 by k in the ion atmosphere comes out to be equal to the diffuse layer thickness let us call it is call this thickness delta. And as you already know, square of k time psi in the equation delta 2 psi by delta x2 is actually equal to minus 4 by raw by D right, where the charge density at a particular point D is the dielectric constant of the medium that is have the Foshan’s equation as a initially illustrated.

So, for this part of the equation the simple solution for this part psi x comes out to be equal to the standard solution Ae to the part of minus kx plus B e to the power of kx in that is how the standard solution to this problem would declared. And we again apply in the same manner the boundary conditions. So, we know that at x equal to infinity in this particular case the potential at infinity is 0 meaning there by that b automatically become 0.

If it is otherwise, at infinity this term is very large the only way you can satisfied this solution is be assuming of a there is b negligible or 0. And simultaneously psi x comes out to be equal to the potential function at point x comes out to be equal Ae to be power of minus kx psi. Simultaneously again, the rah which is actually represented by minus square of k times of psi D psi looking at these 2 parts of the equation can be the written down here as minus A times of square of k times of b by 4 pi e to be power of a minus kx.

So, that is have rah is… and of course, there is a D term here by electric constant and we will have to somehow determine what this ka an identical manner assume in the charge distribution and principle of electronic case of a 1 dimensional ionic form.

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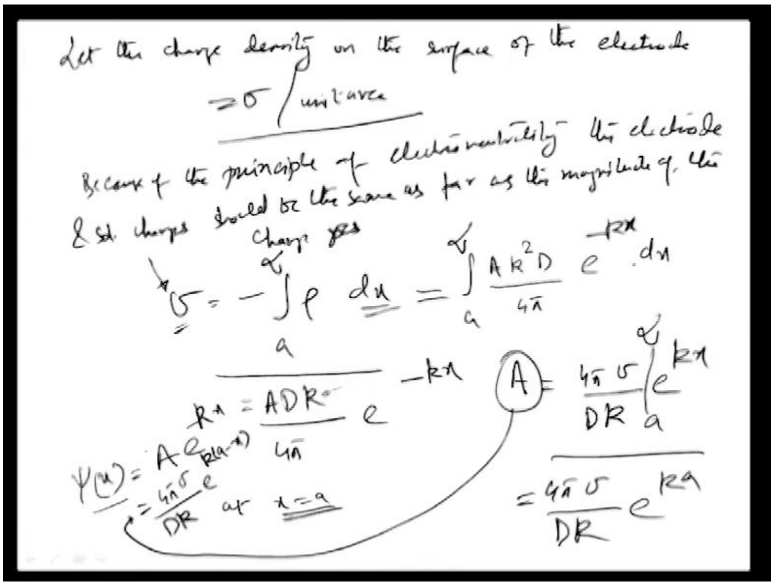

Let the charge density on the surface of the electrode

$= \sigma$ / unit area

Because of the principle of electroneutrality the electrode & sol. charges should be the same as far as the magnitude of the charge

$$\sigma = -\int_a^\infty \rho \, dx = \int_a^\infty \frac{A k^2 D}{4\pi} e^{-kx} . dx$$

$$= \frac{ADk}{4\pi} e^{-ka}$$

$$\boxed{A} = \frac{4\pi\sigma}{Dk} e^{kx} \Big|_a^\infty$$

$$= \frac{4\pi\sigma}{Dk} e^{ka}$$

$$\psi(x) = A e^{k(a-x)} = \frac{4\pi\sigma}{Dk} e \text{ at } x = a$$

So let us assume that the charge should density on the surface of the electrode is actually equal to sigma per unit area. And somehow because of the principle of electro neutrality the electrode solution charges should be the same, as far as the magnitude of the charge course. So sigma therefore, of the of the solution or the electrode can be represented as minus off the volume charge density of the solution times of d x.

Because, available is in the x direction we do not consider any other direction for comparing the sigma value. So, we assume that there is a homogeneity of distribution of charges as we move along each plane along a certain value of x equal to x1 x2 x3 x4, so on up to infinity. So, if you put the value of row here in this equation in try to solve, we actually get you know and this charge density here being positive this is off course a negative charge density negative sine goes away.

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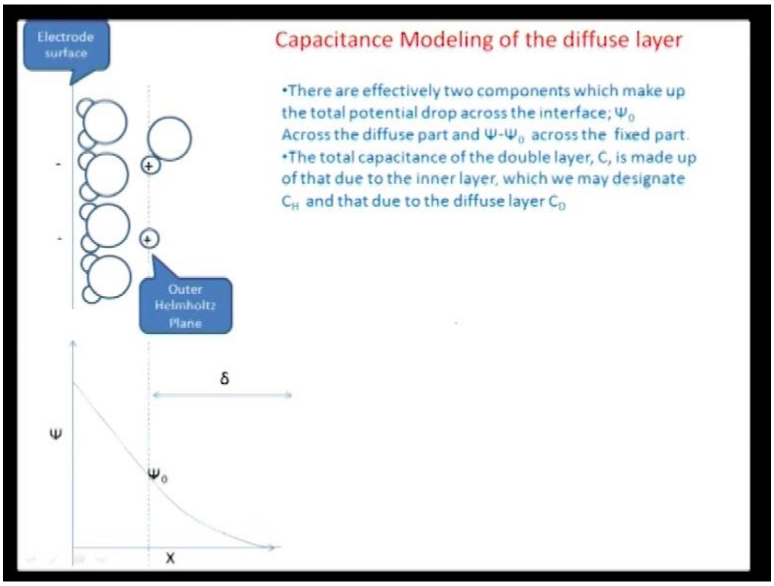

Capacitance Modeling of the diffuse layer

- There are effectively two components which make up the total potential drop across the interface; Ψ_0 Across the diffuse part and Ψ-Ψ_0 across the fixed part.
- The total capacitance of the double layer, C, is made up of that due to the inner layer, which we may designate C_H and that due to the diffuse layer C_D

So, we are able to see this as a to infinity times of a square of k times of D divided by 4 pi to the power of minus kx times of dx and this can further the be expressed as A Dk divided by 4 pi e to the power of minus kx the 1 k term goes here and therefore, A can be further be expressed as 4 pi sigma divided by Dk in to the power of kx positive. At x equal to a which there by means the start of the dual layer this value would be 4 pi sigma by Dk e to the power of ka.

So, that is about the expression regarding a would be and because the term potential functions psi x is related to this Ae to the power of minus kx meaning there by that it is 4 pi sigma divided by Dk in to the power of k times of a minus x. Where obliviously, the expression A the constant comes from this particular term here.

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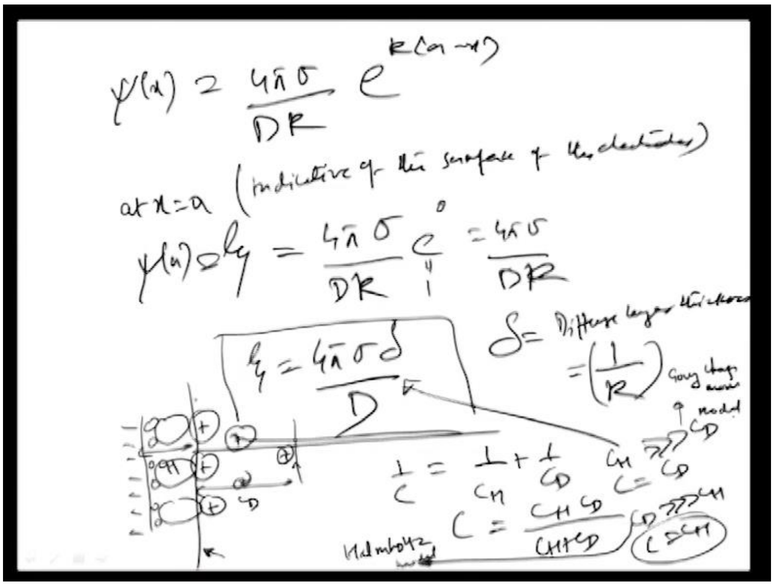

So therefore, we can fully write the potential psi x in these case as 4 pi sigma by Dk in to the power of ka minus x other words, add x equal to a indicative of the surface of the electrode the value of potential function also known as the zeta potential of the surface with respective of solution can be represented as 4 pi sigma by Dk in to the power of 0 is by 4 pi sigma by Dk.

Another words, the zeta potential is basically represented as 4 pi sigma delta D if you may remember delta was the diffuse layer thickness, which had been earlier set to be addicted by the ion association theory was 1 by k. So, that how the zeta potential of any surface comes in to existence on this is very critical value which matters particularly, in electro chemical machining processes.

Because, every surface would have a chart eristic zeta potential with respect to the electrolyte of interest that you're flowing in that zeta potential has to be somehow, crossed over by the applied potential external potential in order to be able to furnish the electro chemical machine in operation. So, zeta potential absolutely important to be kept in mind to estimate things like material removal rate etcetera, which happens normally doing the process of electro chemical machine.

So, if we look at the defuse layer theory were we talk about surface here followed by a inner salvation cell of the i1s which are there in the solution followed by let say a positive ion outer plain here. And then, subsequently a defuse layer which starting from the Helmholtz Outer plane here all the way to the to infinity. We say, that if supposing the capacitance here is capacitance of Helmholtz layer CH and here is CD the overall capacitance which would come into a exist this is actually 1 by CH plus 1 by CD.

Or in other words, c can be represented as CH CD by CH plus CD. Here if supposing CH dominates CD let us say, so then C becomes equal to CD and vise-versa. If CD in to dominates CH C becomes equal to CH. So therefore, this particular module is known as the Helmholtz module is predominance of the diffusely capacitance and this is known is the model. When you talk about the capacitance modeling of a defuse double layer with respective any surface or any solution.

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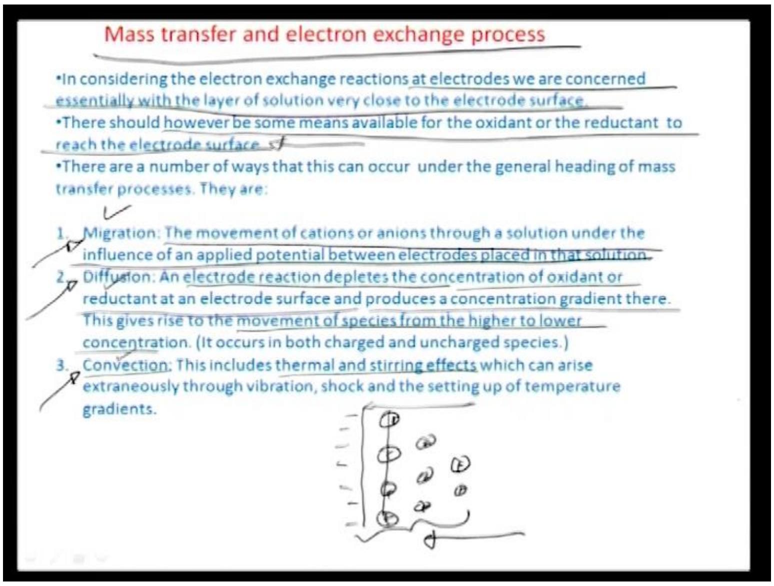

Mass transfer and electron exchange process

- 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, let us look at some aspects of Mass transfer and electron exchange process involved there in. So, in considering the electron exchange reaction at the electrodes we are concerned essentially with the layer of solution very close to the electrode surfaces you've just seen. And model just before and there should be some means; however, available for oxidant or the reductant to reach the electrode surface.

If you look at this interface formulated with this so called double layer defuse and Helmholtz layer. So, this layer hole has to be crossed over for any electro chemical reaction to happen and the way that they are principally done are through 3 process are 3: steps 1 of them is called Migration another is Diffusion and the third is Convection. So, the Migration is the movement of cations or anions through the solution under the influence of an applied potential between electrode place in that solution.

Migration automatically starts happening when, the electrode just about touches the solution and this is the reason for the double layer and then, you have of course the electrode reaction which depletes the concentration of the oxidant of the reductant at an electrode surface. And produces a gradient there in... So, this gives rise to the movement of species from higher to lower concentration talkers in both char is done as char spices.

Then, of course we have Convection which relates to thermal string effect of the solution we can arise extraneously through vibrations, shock and the setting up of temperature gradients. These of the 3 principle mechanism in which the iron scan moves back and forth between the electrode in the solution and cross the double layer does established. That is the mechanism of mass transfer which happens mostly in the even the electro chemical machining processes.

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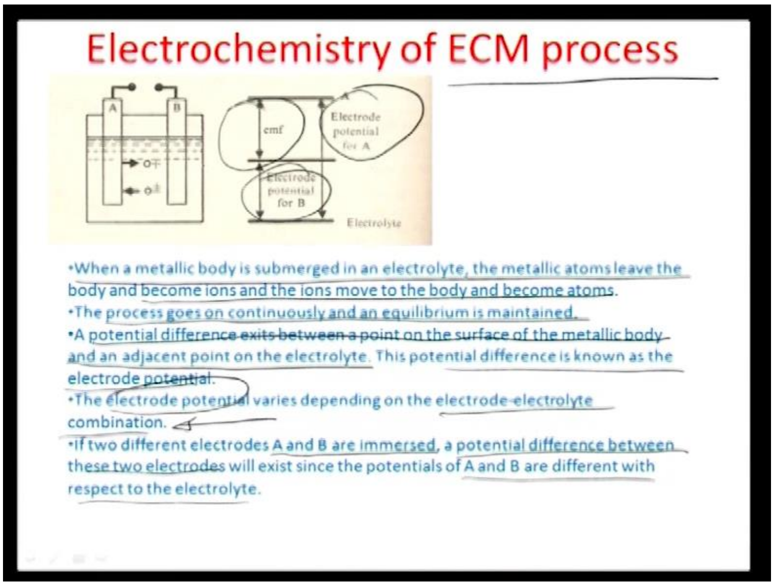

Electrochemistry of ECM process

- •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.

So, let us look at the fundamental of the ECM process here, so when a metallic body.

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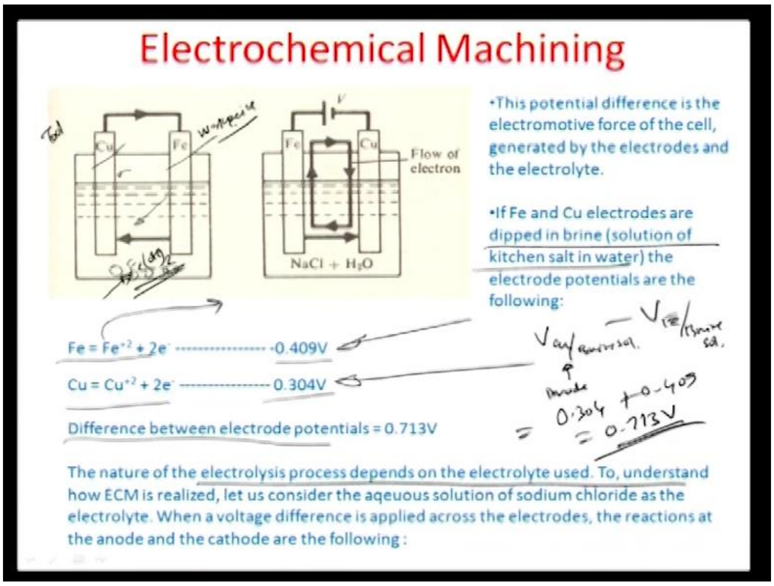

Electrochemical Machining

- This potential difference is the electromotive force of the cell, generated by the electrodes and the electrolyte.
- If Fe and Cu electrodes are dipped in brine (solution of kitchen salt in water) the electrode potentials are the following:

$Fe = Fe^{+2} + 2e^-$ ---------------- -0.409V

$Cu = Cu^{+2} + 2e^-$ ---------------- 0.304V

Difference between electrode potentials = 0.713V

$V_{Cu/brine\ sol.} - V_{Fe/brine\ sol.}$

Anode

$= 0.304 + 0.409$

$= 0.713V$

The nature of the electrolysis process depends on the electrolyte used. To, understand how ECM is realized, let us consider the aqeuous solution of sodium chloride as the electrolyte. When a voltage difference is applied across the electrodes, the reactions at the anode and the cathode are the following :

So, this will sake of a repetition in the ECM process the following events and it actually take place. It start with when a metallic body is submerged and electrolyte metallic atoms leave the body becomes irons are moves to the body and becomes atoms. And the process goes on continuously and then equilibrium maintain. The potential differences exist between a point in the surface of the metallic bossy and an adjusting point on the electrolyte. And this difference is known as the electrode potential.

The electrode potential were is depending on the electrode electrolyte combination. So, this actually is the nothing but the zeta potential that they are mentioning of a surface. And if 2 different electrodes A and B are intern immersed, together semi electrolyte and potential difference given externally between these electrodes. First of all there will be potential difference will automatically exist.

Then, you externally give a potential difference also there would be some kind of transport of irons from the solution into the electrodes or vice versa. And the total amount of electrode you know difference of potential which would does arise is basically, the potential the electrode A minus the potential electrode for B and that would be the net EMF which is available which would create a condition were am start moving is supposing we are not giving any external field or external potential to these set of electrodes. And the in the process supposing if we have 2 electrode copper and ion as mentioned here in brain solution or solution of kitchen salt in water. And you already know that the stranded electrode potential of both.

These reactions were ion gets into state listening 2 electrons minus 0.0409 Volts and copper getting into cypress state and realizing to electronics 0.304 Volts. The difference between electro potentials of the copper and the ion electrode can be represented as the potential of the anode minus the potential of the cathode. So, it is basically potential of the copper brain solution minus the potential of then this basically is anode express state is a placed higher on the electro activity series, potential of Fe with respect to the brain solution. So, therefore, this becomes equal to 0.304 plus 0.409 0.713 Volts.

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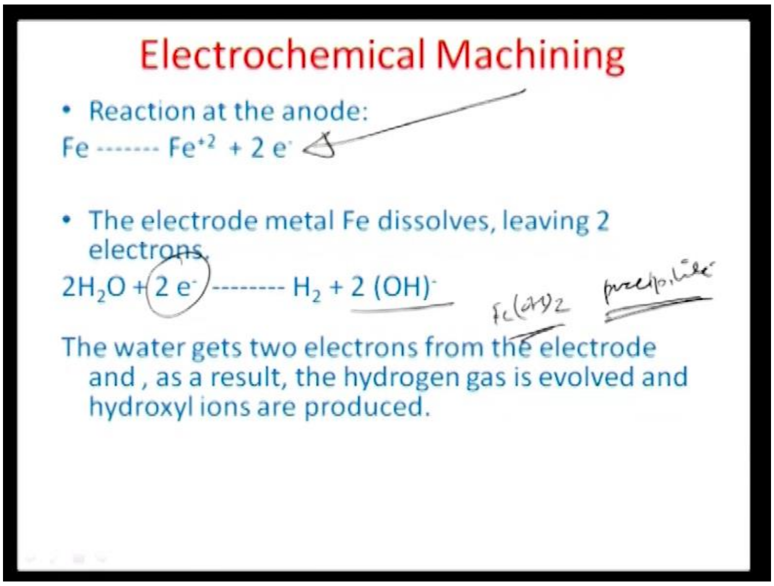

Electrochemical Machining

- Reaction at the anode:

$Fe \text{ ------- } Fe^{+2} + 2e^-$

- The electrode metal Fe dissolves, leaving 2 electrons.

$2H_2O + \boxed{2e^-} \text{ -------- } H_2 + 2(OH)^-$

$Fe(OH)_2$ precipitate

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

The nature of electrolysis a process depends on the electrolyte used and supposing you were to do then, whatever comes out here for example: if Fe plus 2 state come out of this electrode here and being the cathode and this basically, gets converted into immediately into Fe OH2 in this Ferrous hydroxide not dissolvable any more in the solution. So, it prostitutes down it formulates a crystals here.

So, it does not gutter depositor anything else as Metra fact does not get re deposited on the copper. So, this can be the tool and this can be the work piece and this can be bases of electro chemical machine.

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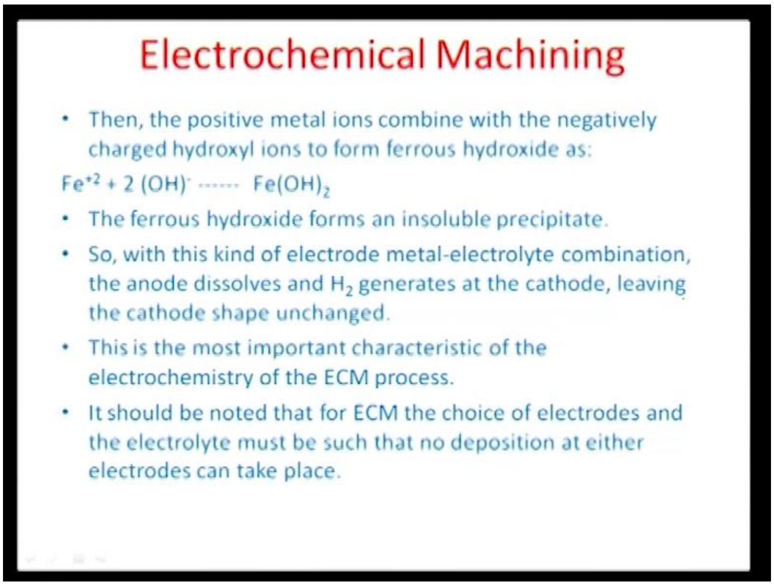

Electrochemical Machining

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

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

- 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.

So, that's what or that is how the Electrochemical Machining is realize these of the reaction for example, the ion get i g and the Hydrogen getting spilt up by the 2 electrons that is released by the ion getting into H2 plus 2H minus and the resultant Fe OH2, which is non-dissolvable is formulated and this is the precipitate which can be later on moved and it finishes the machining operator.

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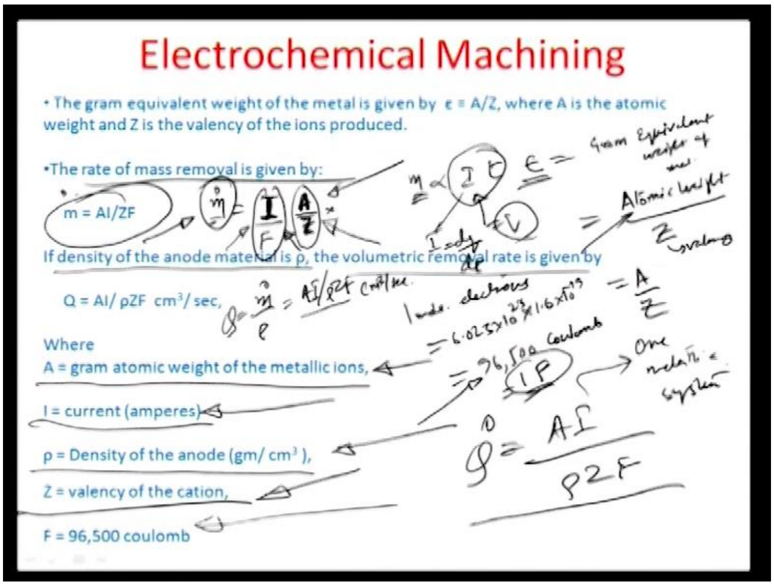

Electrochemical Machining

- 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:

$m = AI/ZF$

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

So, basically let us look at some of the mathematical detail or estimation of the MRR Material Removal Rate using the Faraday's law that we're discuss before. And as you already know that by the Faraday's law the amount of weight that is removed. The amount of wait in grams of material deposited is also given by the, or it is proportional to the ambiance current.

The total time duration for which the current is flown in epsilon which is actually equal to the gram equivalent weight; the gram equivalent weight of a material and by the definition of it the equivalent way it is 1 more mole of the material which is the weight of the 1 mole of material which is also equal to atomic way per unit the valence of the material Z, Z is the valence. So, we can call it A by Z.

And essentially, the amount of charge which would have to be flown in the system is related to this quantity I into t as you know I already the d Q by t the amount of you know the rate of change of charge or rate of flow of charge. So, this is the time integral of I meaning there by this is the total charge and when we are considering 1 mole in 1 atomic weight the total charge that would be involved in removing this 1 mole is basically equal to 1 mole electrons right.

And this 1 mole electrons is 6.023 10 to the power of 23 times of charge of 1 electron which is 1.6 10 to the para of 19 minus 19 would formulate the term 9 to 6500 Columb, which is also known as a Farad, which is also described by the term f. So, this 96500 Columb is the unit for 1 mole charge or 1 mole electrons. So therefore, the mass rate of removal the rate at which the mass or the weight gets resolved or deposited would be equal to the rate at which your flowing charge that is the current times of the equivalent weight that your removing. That is A by Z time of how many mole of current is flowing per unit time represented by the F.

So, I by F is that term right the moles of electrons which are flowing. And so many moles with 1 mole removing A by Z weight of a particular material add a certain rate which is determined by you know this current term here rate of queue flow of charge would be the m dot or the rate of flow of desolation or rate of deposition or rate of flow of material in fact.

Though. so basically, the mas removal rate of ECM process is therefore given by this term m dot AI by ZF just for the sake of repetitions A by Z is the atomic ware of 1 mole of a certain ion and exactly how many moles per in time is being flow in is given by the quantity I by F. And, so you are essentially looking at what is the mass rate which is coming out from the system because of the flow in of this particular charge. So, if you assume further the density of the anode material is rah there can be a estimation of the volumetric removal rate. So, it can be given by m dot by rah.

So, rate of change of mass per at volume for in density during their by the volume which is being by the volume rate is emanated which is being emanated, so this can represent as AI by rah ZF AI by rah ZF and the units of this could been centimeter cube per second. For the sake of repetitions again is gram atomic weight of the metallic iron, I is the current in amperes which you trying to flow and rah is the density of the anode in gram per centimeter cube.

The Z is the valence of the action of interest which is coming out or being deposited and F is off course the amount of charge corresponding to 1 mole electrons given by F; the quantity F of Fared 96500 Columb. So, that is how you can sort of get in estimation of, rate of removal Q dot AI by rah ZF. So, this is only if predominantly 1 metallic system is existing right. But however, most of the real Engineering applications come when there are allied components or many such metals participated in the system. So therefore, we somehow need to tailor this mass removal or volume removal rate in the manner of that it can be applied to alloyed systems.

So, today we are kind of at the end of this lecture, but than in the next lecture we will take this of and try to see that if there is an alloyed system with more than 1 metals participating in the processor this electro chemical removal. And what would be the overall rate based on a sort of average between all the alloys which are there in the system of different densities, different atomic ways, difference valences so on so forth. So, we look at that problem in the next class.

Thank you.