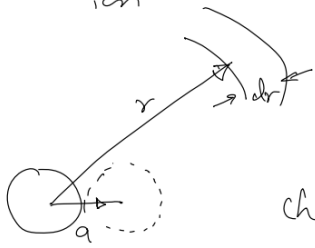


Advanced Machining Processes
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Week - 04
Lecture - 08
Electrochemical Machining-I

We would like to briefly recap what I taught last lecture. So, we were talking about electrochemical machining, some basics and fundamentals. As I would like to just mention here that it is a process where the tool is made the negative electrode, the cathode, and the workpiece is made the anode. And then the choice of electrolyte is done in a manner so that whatever dissolves of the anode goes as a precipitate into the solution, and it is circulated. So, that there is no deposition back on the tool cathode, and this way the whole process is used or is made amenable to machining of materials. So, we also did some estimation of material removal rate, and we studied Faraday's law in the process.

And we were yet to sort of predict what amount of you know material per unit time may be removed by this process when we started looking at the very first important thing in electrochemistry in any electrochemical operation which is an ion transport equation. So, as a part of that equation if you may remember we had actually tried to study what the impact of a positive ion, a central ion of interest would be in assembling its negative charge atmosphere around it. And we studied that what the potential would be at a function at a point A. If we assume that at an infinite distance, there is a charge number density represented by N plus 0 and N minus 0 and near this at a it is N plus and N minus.

For electro neutrality the total -ve charge (assuming the central ion is (+ve) positive) of the atmosphere about a given ion as $-Z_i e$. The total charge in the atmosphere is determined by a spherical shell of thickness dr and distance r from the central ion



$$\int_a^\infty 4\pi r^2 \rho dr = -Z_i e$$

Substituting the value for charge density

$$\rho = -\frac{A k^2}{4\pi} D \frac{e^{-kr}}{r}$$

So, and we try to find out the potential arising out of this situation and the ψ was represented as A square of k by 4π dielectric constant D times of e to the power of minus kr by r . So, that is how ψ a potential at point a would be as a function of r . So, for electro neutrality, the total negative

charge assuming the central ion to be positive of the atmosphere about a given ion is of the atmosphere. And the charge of the central ion be plus $Z_i \epsilon$ in there by meaning that the atmosphere would have a charge of minus $Z_i \epsilon$. So, we can assume that let us say if you have a central ion here and you are looking at some distance r from this ion as if there is a shell of thickness dr around this distance r .

And then you say that there is a distance a or the ion size parameter at which the you know the ion kind of gets 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 interest can be represented as the volume element dV here times of the volume charge density at this point. So, ρ times of dV right and this varies between let us say some distance a all the way to when r goes to infinity. And that can be made equivalent to the charge minus $Z_i \epsilon$ the total charge in the atmosphere around the central ion of interest.

So, dV of course, as you know is nothing but $4\pi r^2 dr$ is d by dr of sort of 4 by 3 pi r^3 . So, that is how this volume element of the shell would be around this whole central charge of you know interest. And so therefore, the volume integral a to infinity of $4\pi r^2$ times of ρ charge density which has been represented earlier you know that ρ has been represented earlier as $A k^2 D e^{-kr}$ by r . So, this charge here A times of 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 $Z_i \epsilon$.

And therefore, we can just simplify this equation. So, let this be equation 1. So, we can simplify this equation further to obtain $A k^2 D$ times of integral a to infinity of $r e^{-kr}$ equals to $Z_i \epsilon$. So, because there is a minus term which comes from the potential the charge density. So, that is the final integral that we have to solve.

$$\int_a^\infty 4\pi r^2 \frac{A k^2 D e^{-kr}}{4\pi r} = Z_i \epsilon$$

$$A k^2 D \int_a^\infty r e^{-kr} = Z_i \epsilon$$

Integrating this expression by parts

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

$f(x) = r$ $g'(x) = e^{-kr}$ (lets assume)

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

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

So, we have to integrate this expression by parts. As we know that you know the formula of integration by parts is $\int_a^b f(x) g'(x) dx = f(x) g(x) \Big|_a^b - \int_a^b f'(x) g(x) dx$. And here as we know that $f(x)$ equal to r and $g'(x)$ or $g'(x)$ x if we assume it has e to the power of minus kr thereby meaning that $g(x)$ can be equal to minus e to the power of minus kr by r . So, we can actually write this whole expression by parts as integral a to infinity $r e^{-kr}$ as minus $r e^{-kr}$ 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 a e to the power of minus ka by k plus e to the power of minus ka by square of k.

And simultaneously we can have A square of k times of D times of e to the power of minus ka by k, because we are just substituting this result into the equation formulated earlier here the equation 1. So, it has been just the same equation formulated earlier. So, therefore e to the power of minus ka by k times of square of k times of ka plus 1 equals Zi epsilon or in other words, as you already know that the potential function Zi is A e to the power of minus kr by r and A from here can be found out as square of k goes 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 Zi can be represented as Zi epsilon D to the power of or D times of 1 plus ka times of r times of e to the power of minus k or let us say plus ka 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 centre of the ion. So, that is the concept of a point charge that the charge is concentrated at a point, but then it can have a radius 0 to a. So, at a the potential because of the charge which is somewhere here or 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 is equal to 0 sorry 1.

$$\begin{aligned} & \therefore \int_0^a r e^{-kr} dr \\ &= \frac{r e^{-kr}}{-k} + \frac{e^{-kr}}{k^2} \\ & \therefore A k^2 D \left[\frac{e^{-ka} (ka + 1)}{k^2} \right] = Z_i \epsilon \\ & A = \frac{Z_i \epsilon e^{ka}}{D [1 + ka]} \quad \& \quad \psi = A \frac{e^{-kr}}{r} \\ & \qquad \qquad \qquad = \frac{Z_i \epsilon e^{ka} e^{-kr}}{D [1 + ka] r} \end{aligned}$$

So, therefore, that is how the potential at a 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 a look into what all components would go in formulating a potential at the point a. So, here let us say the psi therefore, at r equal to a can be written down as Zi epsilon by D times of 1 divided by a times of 1 plus ka meaning thereby it can be Zi epsilon by D times of 1 by A minus k by ka plus 1. This is how could happen when it is resolved into partial fractions and we can represent this as Zi epsilon by D a minus k times of Zi epsilon by D times of 1 plus ka and this can further be expressed as

plus-minus Z_i epsilon by D a minus plus depending on the value of the charge $k Z_i$ epsilon by D times of $1 + ka$. So, just by the look of it appears as if this can be the effect of the central positive ion and this component because it is exactly the opposite of it can be the effect of the charge atmosphere which is principally negative charge.

$$\begin{aligned}
 \text{As } r \rightarrow a \\
 \psi &= \frac{Z_i \epsilon}{D} \frac{1}{a(1+ka)} \quad (\text{resolving into partial fractions}) \\
 &= \frac{Z_i \epsilon}{D} \left[\frac{1}{a} - \frac{k}{(1+ka)} \right] \\
 &= \frac{Z_i \epsilon}{D a} - \frac{k Z_i \epsilon}{D(1+ka)} = \frac{+Z_i \epsilon}{D a} + \frac{-k Z_i \epsilon}{D(1+ka)} \\
 \text{Equivalent} &= \parallel \quad \parallel \\
 \frac{q \times 1}{\epsilon_0 a} & \text{ ion itself} \quad \parallel \quad \text{Due to its ion atmosphere} \\
 &= +ve \text{ energy} \quad \parallel \quad \text{atmosphere} \\
 & \text{is due to ion itself}
 \end{aligned}$$

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 $1 + ka$ 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 of some relevance because we will try to utilize this in order to find out what is the potential of such a surface which would get which is nothing but an assemblage on assemblage of the charges of 1 type with respect to the charges of other type which is present lined up as the Helmholtz layer near the surface as a dual layer. So, this ion atmosphere would become very relevant in calculating the zeta potential of the surface at that stage, but you do understand that the contribution of the ion atmosphere onto the ion's surface also is of equal amount of significance and relevance in this particular illustration. So, let us now look at some of the very basic fundamentals of what happens when an electrode is dipped in a solution which creates an assembly of the charges.

So, let us now look into a slightly different aspect of the double layer as I was mentioning before. So, how does the double layer get formulated? Let us say this is the electrode surface that we are looking at and this zinc and this is immersed in just a brine solution NaCl plus H_2O salt water. And so, there is an automatic tendency of the zinc to formulate zinc ions. So, they would actually be ions of zinc which would come out in dissolved manner from the electrode and there would be water molecules which would be immediately encircling the zinc so-called. So, this is the water molecule encircling the zinc and that is how this whole orientation would be.

So, each of the zinc atom is surrounded by a bunch of water molecules and that is true for all the zinc atoms which are there in the solution. And correspondingly there are negative ions which are there on the electrode side. So, there are positive ions in the solution and the negative ions in the electrode side. 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 as ions into the solution should have charge wise the similar amount of electrons on the electrode surface. So, what is important

and worth here to mention is that there is a thin layer of water which would come between the positive charges and the ions separating them from each other.

And thus, the zinc plus 2 cannot get deposited back on to the electrons and this becomes electron-rich and there is a field which exists between the you know the first layer of zinc ions which are here 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 the solution charge that is number 1 and then ions from the solution may approach the electrode surface only so far as their inner solvation shells. So, solvation shell is this shell which is formulated because of the water molecules around the zinc plus 2 atom. So, as much as this solvation shell can allow only that much distance the ion can have in proximity to the electrode charge electronic charge which is on the electrode. So, 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 and this is known as the outer Helmholtz plane is indicated here. So, this is an assemblage of all the zinc plus 2 atoms hold on to a certain line and the size of ions formulating the outer Helmholtz plane are larger and the total number of ions needed to do a complete charge balance cannot all be fitted on this plane. So, obvious reasons that electron here in the electrode is part of the electronic structure much more densely packed in comparison to the ions which are in the solution which are positive ions. So, therefore, not 1 layer, but subsequently a set of layers would be needed for. So, for example, let us suppose this is the electrode surface and you have negative charge assembly here in the electrode surface.

So, the first set of Zn 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. So, it is sort of atomically impregnated into the surface these electrons and these are full-size ions in the solution. So, there has to be subsequent layers which would be responsible for whatever field escapes this first line of ions and then slowly the field gets neutralized, and the ion layers get thinner and thinner as you go radially from the electrode into the solution. So, typically this layer in 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 right here is sort of a diffuse layer of charges and therefore, in electrochemistry mostly there is a Helmholtz layer and then there is a diffuse layer which has its own 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 the ions from getting back into the electrodes back 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 charges are all held as you know with increasing order-disorder in the outward direction into the solution and this is known as the diffuse layer of charges.


So, that is why double layer. So, you have 1 layer which is the Helmholtz layer, and another layer which is the diffuse layer of the charges. So, that is how in a nutshell the you know the whole electrode is oriented with reference to the solution. So, let us actually now look into how the potential zeta would vary with respect to distance from the electrode surface. So, if you plot the

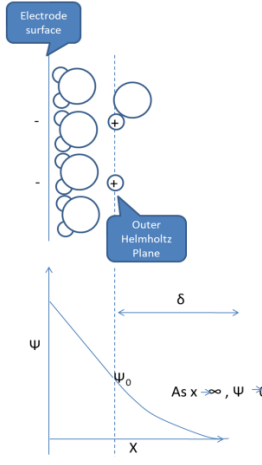
potential zeta with respect to x the distance into the solution as you can see the potential varies linearly like this all the way up to this value here which is actually as I will later on tell you the zeta potential of the surface. And then after that the moment it crosses the outer Helmholtz plane the potential starts varying of the diffuse layer in a different manner it is not a it is a non-linear behavior in this particular zone.

So, we have to somehow be able to find out what this potential function is with respect to x and as obviously, as we have done before at x equal to infinity the potential function zeta is actually equal to or psi is actually equal to 0. So, this calls for the solution of the Debye Huckel theory in 3 dimensions as we did just about few slides back in an ion solution to a 1D case. A 1D is only the dimension of interest from the array of ions which are somewhere here on the electrode. So, this is the array of ions and with respect to that array of ions maybe we can consider this all focused on to a single place with respect to this 1 let us say central ion as an array available as an array format on the electrode. What is the distribution of the charge in the solution and thereby the potential function would be recalled in that case.

So, it is simply a 1-dimensional approximation of the Poisson's equation we can just write $\nabla^2 \psi$ by $\frac{d^2 \psi}{dx^2}$ is actually equal to square of k times of psi as you already know from earlier equation. This square of k is basically the function which comes in terms of $\frac{\sigma}{\epsilon_0 \epsilon_r K T}$ times of so on so forth. So, that is what the k-square term is here. Also what is of interest and significance is that as we found out last time that with respect to the central ion there is an effective radius of the ion atmosphere and this effective radius was given by $1 + k a$ by k. In other words, it means it was $1 + k a$.

The Electrode Double layer





The diagram illustrates the electrode double layer. On the left, an 'Electrode surface' is shown with a layer of negative charges (represented by minus signs and circles). To its right is the 'Outer Helmholtz Plane' (OHP), also with negative charges. Further right, positive ions (represented by plus signs and circles) are distributed in the solution. A graph below shows the potential ψ as a function of distance x from the electrode surface. The potential starts at ψ_0 at the electrode surface and decays towards zero as x increases. A distance δ is marked from the electrode surface to the OHP. A note states: 'As $x \rightarrow \infty, \psi \rightarrow 0$ '.

- 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 Huckel 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)

$\therefore \frac{d^2 \psi}{dx^2} = \kappa^2 \psi$

have 1 to come out to be the effective ion radius of the surroundings

So, that was the radius of the effective surrounding ion atmosphere with respect to the central charge of interest. So, we will consider the similar value here and try to see what this function results in. So, by this theory of ion association, I would just like to just simply state it without really getting into the proof of it, but by the ion association theory, the value of $1 + k a$ in the ion atmosphere comes out to be equal to the diffuse layer thickness. Let us call this thickness delta and as you already know square of k times psi in this equation $\nabla^2 \psi$ by $\frac{d^2 \psi}{dx^2}$ is actually equal to

minus $4\pi\rho$ by D right, where ρ is the charge density at a particular point d is the dielectric constant of the medium that is how the Poisson's equation was 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 $Ae^{-kx} + Be^{kx}$ that is how the standard solution to this problem would look like.

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 thereby that B automatically becomes 0 because otherwise at infinity this term is very large. The only way you can satisfy the solution is by assuming a very small B negligible or 0. And simultaneously the $\psi(x)$ comes out to be equal to the potential function at point x comes out to be equal to Ae^{-kx} . Simultaneously again the ρ which is actually represented by minus square of k times of $\psi(x)$ by 4π looking at these 2 parts of this equation come can be written down here as minus A times of square of k times of D by $4\pi e^{-kx}$.

So, that is how ρ is and of course, here is a D term here dielectric constant. And we will have to somehow determine what this k is in an identical manner assuming a charge distribution and principle of electron neutrality as we did in the case of a 1-dimensional ionic form. So, let us assume that the charge density on the surface of the electrode is actually equal to σ per unit area. And somehow because of the principle of electro the electrode and solution charges be the same as far as the magnitude of the charge goes. So, σ , therefore, of the solution or the electrode can be represented as minus of the volume charge density of the solution times of dx .

Because the only variation available is in the x direction we do not consider any other direction for comparing the σ 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 x_1, x_2, x_3, x_4 so on up to infinity. So, if we put the value of ρ here in this equation and try to solve we actually get you know and this charge density here being positive this is of course, the negative charge density negative sign goes away. So, we are able to see this as a to infinity times of a square of D sorry square of square of k times of D divided by $4\pi e^{-kx}$ times of dx . And this can further be expressed as a Dk divided by $4\pi e^{-kx}$ the $1/k$ term goes here.

And therefore, A can further be expressed as $4\pi\sigma$ divided by $Dk e^{-ka}$ positive. At x equal to a which thereby means the start of the double layer this value would be $4\pi\sigma$ by $Dk e^{-ka}$. So that is about the expression regarding A would be and because the term potential $\psi(x)$ is related to this Ae^{-kx} I am sorry minus kx meaning thereby that it is $4\pi\sigma$ divided by $Dk e^{-kx}$. Where obviously, the expression A the constant comes from this particular term here. So, therefore, we can fully write the potential $\psi(x)$ in this case as $4\pi\sigma$ by $Dk e^{-kx}$.


Other words at x equal to 0, x equal to I am sorry x equal to an indicative of the surface of the electrode the value of potential function also known as the zeta potential of a surface with respect to a solution can be represented as $4\pi\sigma$ by $Dk e^{-k\delta}$. So, it is $4\pi\sigma$ by Dk . In other words, the zeta potential is basically represented as $4\pi\sigma\delta$ by D . If you may remember δ was the diffuse layer thickness which had been earlier said to be predicted by the

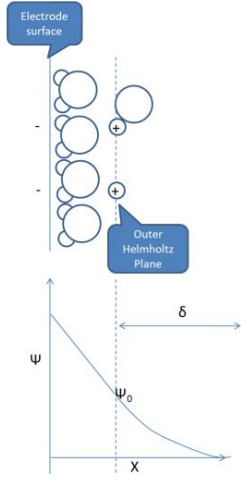
ion association theory as $1/k$. So, that is how the zeta potential of any surface comes into existence and this is a very critical value which matters particularly in electrochemical machining processes.

Because every surface would have a characteristic zeta potential with respect to the electrolyte of interest that you are going in and that zeta potential has to be somehow crossed over by the applied potential, external potential in order to be able to furnish the electrochemical machining operation. And so, the zeta potential is absolutely important to be kept in mind and to estimate things like material removal rate, etc which happens normally during the process of electrochemical machining. So, if we look at the diffuse layer theory where we talk about let us say a surface here followed by a inner solvation shell of the ions which are there in the solution followed by let us say a positive ion outer plane here. And then subsequently a diffuse layer which is 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 C_H and here is C_D the overall capacitance which would come into existence is actually $1/C_H + 1/C_D$ or in other words, C can be represented as $C_H C_D / (C_H + C_D)$.

Here if supposing C_H dominates C_D , C_H is dominating C_D let us say. So, then C becomes equal to C_D and vice versa if C_D predominates C_H C becomes equal to C_H . So, therefore, this particular model is known as the Helmholtz model, it was the predominance of the diffuse layer capacitance and this is known as the Guy Chapman model. When you talk about you know the capacitance modelling of a diffuse double layer with respect to any surface or any solution. So, let us look at some aspects of mass transfer and electron exchange process involved there in.

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 $\Psi - \Psi_0$ 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

$$\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_D}$$

$$C = \frac{C_H C_D}{C_H + C_D}$$

Guy Chapman Model

if $C_D \ll C_H$ $C \approx C_D$ (diffuse layer)

if $C_D \gg C_H$ $C \approx C_H$ (Helmholtz)

So, in considering the electron exchange reaction at the electrodes we are concerned essentially with the layer of solution very close to the electrode surface as you have just seen and model just before. And there should be some means, however, available for oxidant or the reductant to reach the electrode surface. And if you look at this interface formulated with this so-called double layer diffuse and Helmholtz layer. So, this layer has to be crossed over for any electrochemical reaction to happen. And the way that they are principally done are through 3 processes or 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 a solution under the influence of an applied potential between electrodes placed in that solution. And 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 or the reductant at an electrode surface and produces a gradient therein. So, this gives rise to the movement of species from higher to lower concentration it occurs in both charged and uncharged species. And then, of course, we have convection which relates to thermal or stirring effects of the solution can arise extraordinarily through vibrations, shock, and setting up of temperature gradient.

These are the 3 principle mechanisms in which the ions can move back and forth between the electrode and the solution and cross the double layer that is established. And that is the mechanism of mass transfer which happens mostly in the even the electrochemical machining processes. So, let us look at the fundamental of the ECM process here. So, when a metallic body . So, just for the sake of repetition in an ECM process, the following events actually take place.

It starts with when a metallic body is submerged in an electrolyte metallic atoms leave the body becomes ions, ions move to the body and becomes atoms. The process goes on continuously and equilibrium is maintained. The potential difference exists between a point on the surface of the metallic body and an adjacent point on the electrolyte and this difference is known as the electrode potential. And the electrode potential varies depending on the electrode-electrolyte combination. So, this actually is the nothing but the zeta potential that they are mentioning of a surface.

Electrochemistry of ECM process

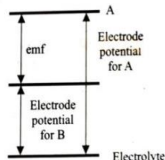
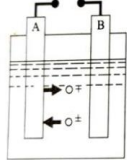


Fig. Material dissolution and deposition **Fig. Cell emf**

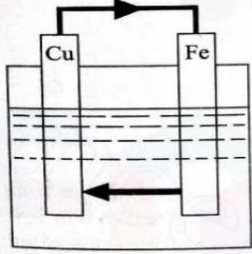
- When a metallic body is submerged in an electrolyte, the metallic atoms leave the body and become ions and the ions move to the body and become atoms.
- The process goes on continuously and an equilibrium is maintained.
- A potential difference exists between a point on the surface of the metallic 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.

And if 2 different electrodes A and B are in turn immersed together in the same electrolyte and potential difference is given externally between these electrodes. First of all, there will be a potential difference will automatically exist and then you can externally give a potential difference also. There would be some kind of transport of ions from the solution into the electrodes or vice versa. And the total amount of electrode you know difference of potential which would thus arise is basically the potential of the electrode A minus the potential electrode for B. And that would be the net EMF which is available which would create a condition where ions start moving.

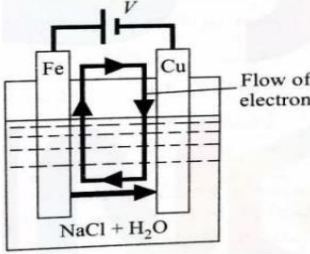
Supposing we are not giving any external field or external potential to these set of electrodes. And in the process supposing if you have 2 electrodes copper and iron as mentioned here in brine solution or solution of kitchen salt in water. And you already know that the standard electrode potentials of both these reactions where iron gets into ferrous state releasing 2 electrons is minus 0.409 volts and copper getting into cuprous state and releasing 2 electrons is 0.304 volts. The difference between electrode potentials of the copper and the iron electrode can be represented as the potential of the anode minus the potential of the cathode. So, it is basically potential of the copper brine solution minus the potential of the this basically is anode. It is placed higher on the electro-activity series potential of Fe with respect to the brine solution.

So, therefore, this becomes equal to 0.304 plus 0.409, 0.713 volts. And the nature of electrolysis process depends on the electrolyte used and supposing if you were to do ECM then whatever comes out here for example, if Fe plus 2 state comes out of this electrode here and being the cathode. And this basically gets converted into immediately into FeOH₂. This ferrous oxide hydroxide is not dissolvable anymore in the solution.

Electrochemistry of ECM process



Case without extra source of emf



Case with extra source of emf

Flow of electron

- 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,

$\text{Fe} \rightleftharpoons \text{Fe}^{2+} + 2e^{-} \rightarrow -0.409 \text{ volt}$ $\text{Cu} \rightleftharpoons \text{Cu}^{2+} + 2e^{-} \rightarrow +0.304 \text{ volt}$ <p style="margin-top: 5px;">difference between electrode potentials = 0.713 volt</p>	<p style="color: #0070c0; font-size: small;">The nature of the electrolysis process depends on the electrolyte used. To, understand how ECM is realized, let us consider the aqueous solution of NaCl as the electrolyte.</p> <p style="color: #0070c0; font-size: small;">When a voltage difference is applied across the electrodes, the reactions at the anode and the cathode are the following,</p>
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So, it precipitates down it formulates as crystals here. So, it does not get redeposited or anything else as a matter of fact does not get deposited on the copper. So, this can be the tool, and this can be the workpiece, and this can be a basis of electrochemical machine. So, that is what or that is how the electrochemical machining is realized. These are the reactions for example, the iron getting removed and the hydrogen getting split up by the 2 electrons that is released by the iron getting into H₂ plus 2H minus. And the resultant FeOH₂ which is non-dissolvable is formulated and this is the precipitate which can be later on removed and it furnishes the machining operation.


So, basically let us look at some of the mathematical details or estimation of the MRR or material removal rate using the Faraday's laws that we have discussed before. And as you already know that by the Faraday's laws the amount of weight that is removed. The amount of weight in grams of material dissolved or deposited is also given by the is proportional to the ambient current. The

total time duration for which this current is flown, and epsilon is actually equal to the gram equivalent weight. The gram equivalent weight of a material and by the definition of it the equivalent weight is 1 mole of the material which is the weight of the 1 mole of material which is also equal to the atomic weight per unit the valency of the material Z, Z is the valency.

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 is dq by dt the amount of you know the rate of change of charge or rate of flow of charge. And so, this is the time integral of I meaning thereby 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.

And this 1-mole electrons is 6.023×10^{23} times of charge of 1 electron which is 1.6×10^{-19} would formulate the term 96500 Coulomb which is also known as a Farad which is also described by the term F. So, this 96500 Coulomb 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 you are flowing charge that is the current times of the equivalent weight that you are removing that is A by Z times of how many moles of current is flowing per unit time represented by the F.

Electrochemical Machining



- The gram equivalent weight of the metal is given by $\epsilon = A/Z$, 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

$$Q = AI/\rho ZF \text{ cm}^3/\text{sec},$$

Where
A = gram atomic weight of the metallic ions,
I = current (amperes)
 ρ = Density of the anode (gm/ cm³),
Z = valency of the cation,
F = 96,500 coulomb

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 at a certain rate which is determined by you know this current term here rate of flow of charge would be the m dot or the rate of flow of dissolved dissolution or rate of deposition or rate of flow of material in fact. So, basically the mass removal rate of an ECM process is, therefore, given by this term m dot A I by Z F. Just for the sake of repetition A by Z is the atomic weight of 1 mole of a certain ion, and exactly how many moles per unit time is being flown 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 flowing of

this particular charge. So, if we assume further that the density of the anode material is ρ there can be estimation of the volumetric removal rate.

So, it can be given by $m \dot{V} = \rho$. So, rate of change of mass per unit volume or per unit density giving thereby the volume which is being emanated or the volume rate which is being emanated. So, this can be represented as $A I = \rho Z F$ and the units of this could be in centimetre cube per second. For the sake of repetition again A is the gram atomic weight of the metallic ion, I is the current in amperes which you are trying to flow and ρ is the density of the anode in gram per centimeter cube. Z is the valency of the cation of interest which is coming out or being deposited and F is of course, the amount of charge corresponding to 1 mole electrons given by F the quantity F of Farad 96500 coulombs. So, that is how you can sort of get an estimation of the volume rate of removal $Q \dot{V} = A I = \rho Z F$.

So, this is only if predominantly 1 metallic system is existing. But however, most of the real engineering applications come when there are alloyed components, or many such metals are participative in the system. And so, therefore, we somehow need to tailor this mass removal or volume removal rate in a manner. So, that it can be applied to alloyed systems. And so, today we are kind of at the end of this lecture, but then in the next lecture, we will take this up and try to see that if there is an alloyed system with more than one metals participating in the process of this electrochemical removal. Then 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 weights, different valencies so on so forth. So, we look at that problem in the next class. Thank you.