BioMEMS and Microfluidics
Prof. Dr. Shantanu Bhattacharya
Department of Mechanical Engineering
Indian Institute of Technology, Kanpur

Lecture – 06

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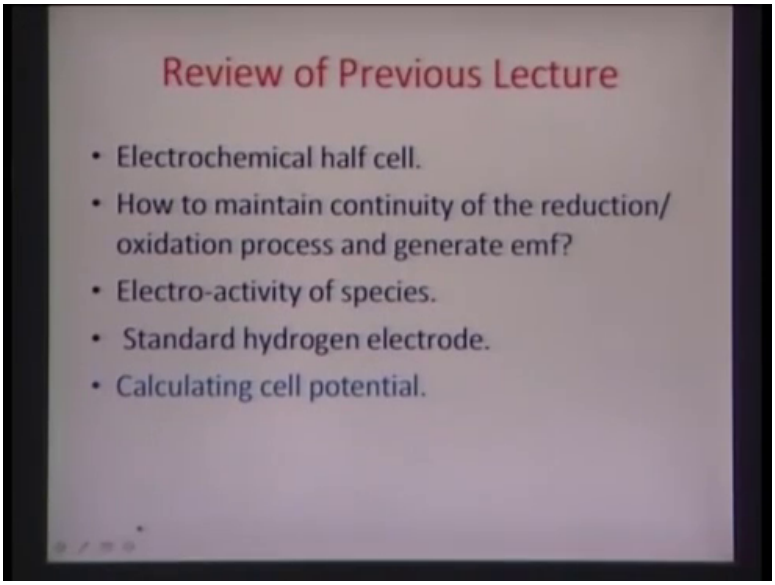

Welcome back. I would like to review what we did last time. Last time we talked about the electrochemical half cells and we also discussed about how to maintain continuity of the reduction oxidation process. If you remember there was a lump of zinc. If you put in a copper sulphate solution and immediately to be covered with the metal copper, metallic copper to which there won't be any reaction any further and in order to maintain the continuity, we basically tried to connect two half cells. One zinc where was a salt solution of zinc and copper was independently in another salt solution of copper. Then, we connected both the solution only through a salt bridge and both the electrodes with the. Basically that kind was useful maintaining between continuous flows of electrons. Therefore, generated often a current.

We also talked about electro activity of species, basically the ability of a particular metal to displace hydrogen from water theme or acid, and essentially this is very important aspect of electro chemistry because we kind of know an order in which what would displace what from its corresponding salt solution. We also talked about a relative absolute potentials and we discussed the standard hydrogen electrode which essentially a platinum electrode dipped in a one molar H_2O solution in water last forming hydrogen H_3O plus, where hydrogen was

bubbled through about 1 atmospheric pressure and the temperature was maintained about 25 degree celcius or so.

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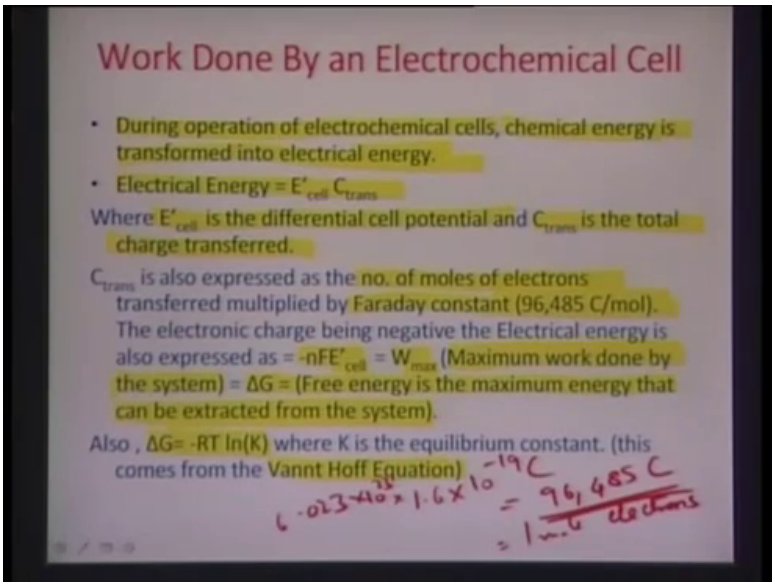

So, then we started just about calculating cell potentials and they are the main question that needs to be addressed is, how can be we really have an idea of relationship between in the concentration of an analyte and EMF that it would generate? So, for that we will be actually deriving something which we have commonly known as the Nernst equation. So, let me look through how this derivation is done. I would typically like to derive this through the fundamental principles of chemistry and then, go ahead with utilizing this Nernst equation to calculate the concentrations of different analytes of interest. So, in order to start with, we really need to find out what is the total work done by an electrochemical cell that we have discussed yesterday.

So, as we know there is a potential difference between the anode and the cathode. Anode is essentially where the oxidation reaction happens; the cathode is where the reduction actually happens and due to this a potential difference and owing to this difference, there is a flow of charge across the circuit from the cathode, from the anode to the cathode, that is electron flow and correspondingly, there is you can say that the conventional current direction is from the cathode to the anode. So, that is work essentially which the cell does in order to transfer some electrons from one electrode to other, and the amount of electrical energy that is essentially spent during this operation of an electrochemical cell is, I am sorry let me just go ahead and give me a minute.

So, essentially when we talk about work done from by an electrochemical cell during this operation of charge transfer, the chemical energy which is stored in form of the salt solution with the particular metal is transformed into electrical energy, and the total amount of electrical energy in these processes e dash cell into c trans, where c trans is the total charge that is transferred from one electrode to another, and e dash cell is the differential cell potential between both the electrodes. So, we can also express this in a little different manner by assuming that n number of moles of electrons had really crossed from one electrode to another. Essentially there is the famous faraday constant which is corresponding to the charge of one of mole electron. So, as we all know that the electronic charge is around 1.6×10^{-19} Coulombs and if you multiply this with one mole, the Avogadro number 6.033×10^{23} . You get this 96485 coulomb.

So, essentially this value is the charge for one mole electrons. So, if you have n mole electrons which are crossing from one electron to another, the c trans which is the total amount of charge so-crossed is also known as, also given as n f and this is a negative charge. So, you have a negative sign which comes up. So, this charge is transferred and there are potential e dash cell and that is essentially what the maximum work done is of this system. So, this electrochemical cell, essentially the processes of a charge transfer of n f value and there are self-potential $E_{cell}^{'}$ makes or contributes maximum work given by $-nF\,E_{cell}^{'}$. So, from principles of thermodynamics, we also know this very famous Gibbs free energy concept which is essentially the maximum energy that can be extracted from system and that can be equated to the maximum work done by the system. So, really in the Gibbs free energy delta g which is also given by this expression here minus r t l and k, and in case the equilibrium constant I am going to come just about in a little bit. This essentially this expression comes from Vannt Hoff equation. We will just do this in a little bit, but what I am trying to say here is ΔG of any free cell are the free energy of any free cell is also equal to the maximum work that can be done by the free cells. The $\Delta G = -nF\,E_{cell}^{'}$ and is also can be presented as $-RT\,lnK$.

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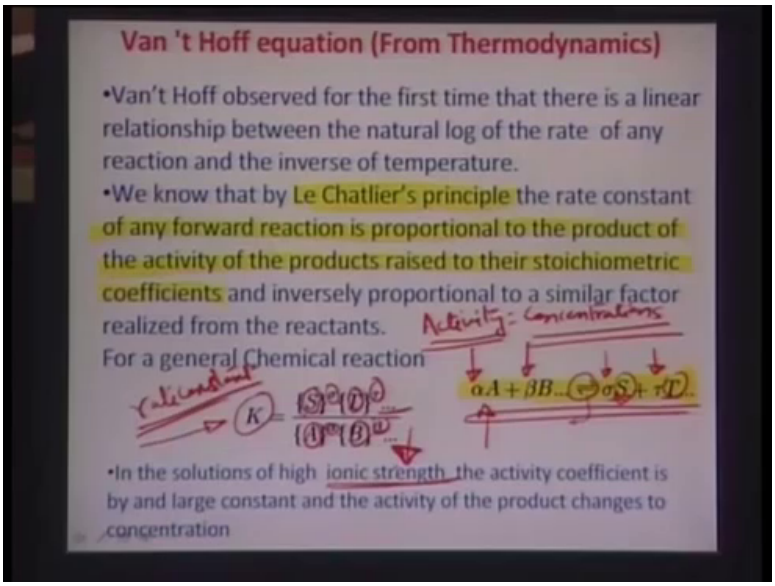

So, let us look at the Van't Hoff equation and how it came from thermodynamics. So, the Van't Hoff for the first time observed that there is a linear relationship between the natural log of the rate of reaction and the inverse of temperature. In the rate of a reaction again assuming this to be the reaction, alpha moles of A reacts with beta moles of B, and with several other components here, reversibility obtains sigma moles as thermal of C and several other products here. So, by Le Chatlier's principle you can really find out the rate constant of any such reaction. What this principle says is that the rate constant of any forward reaction is proportional to the product of the activity of the products raised to their stoichiometric co-efficient. A stoichiometric coefficient here being alpha as you see here in this beta, so how many moles are participating in a sigma and a tau. So, this is what the stoichiometric coefficients of these different reactions are. So, therefore, Le Chatlier's principles says that the rate constant of any forward reaction is proportional to the product of the activity all that you know of the product raise to stoichiometric coefficient.

$$\alpha A + \beta B \rightleftharpoons \sigma S + \tau T$$

$$K = \frac{[S]^{\sigma} T^{\tau}}{A^{\alpha} B^{\beta}}$$

So, here I am just about to explain what activity here means. At this time let us just consider it to be equal to the concentration. So, activity essentially is a term which is a factor of the concentration of a particular analyte and I will be explaining this in a great details later because for designing electrodes, we should be able to do electro chemicals BioMEMS and

devices, we need to find out some times the activity of a ion of interest rather than the concentration of man of interest. So, essentially Le Chatlier's principle the rate constant of any forward reaction is proportional to the product of the activity of the products. That means, S and T here at the products of the reaction right and it is a multiplication of the product of the activity of s and t, that is the products of reaction raise to their stoichiometric coefficient sigma and tau and the others and divided by the activity of the reactants of this particular reaction is to power of their stoichiometric coefficient which is alpha and beta.

So, for any general chemical reaction, this is how the equilibrium constant of the rate constant of a particular reaction can be found out. So, this is what a critical parameter is to study any redox reaction reduction, oxidation reaction and essentially the change in 1 like let say the change in the reacting side. I would essentially need to shift in the equilibrium and there would be an increase in the forward rate. So, what would happen is that more of a, would be converted into s or t and therefore, the equilibrium would shift back to its normal. So, any disturbance on any sides in terms of concentration of the reactants of the products would lead to a shift of the equilibrium position and this equilibrium would try to get back to normal c. That is how these redox couples really work.

So, in the solutions of high ionic strength, the activity coefficient is by and large constant and the activity of the product changes to the concentration. So, we really bother about those situations where the ionic strength may not be very huge, and that is really the case in some of the samples of interest or the analysts of interest that we try to measure using BioMEMS architecture because this ion strength sometimes is not in control. Therefore, how do we really measure very accurately the you know the EMF and correlate that to the concentration of an analyte which has a low ionic strength is the challenge, and for that there are certain rules and protocols which are followed, so that in linearity sense we can make a repeatable measurement and correlate that EMF of such product, of such a reaction to the concentration of one of the analyte of interest.

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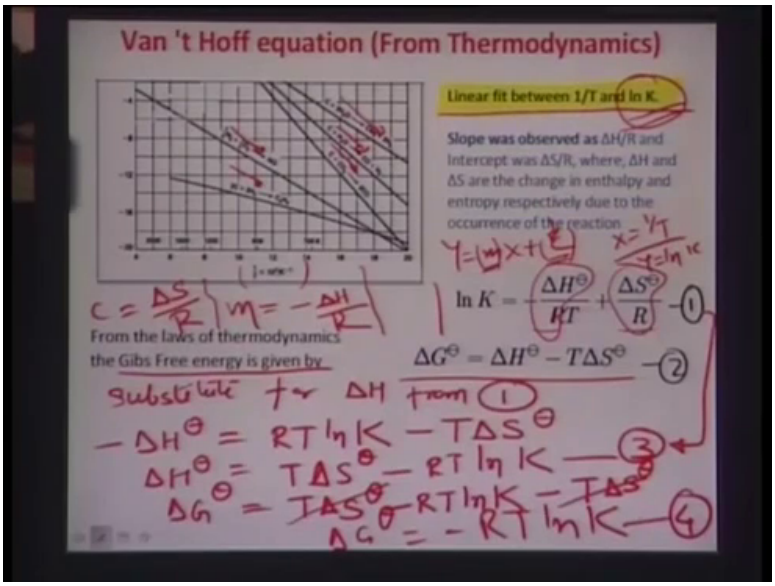

So, what essentially Van't Hoff did is, he plotted experimentally you know the rate constant, the natural logs of the rate constant ln K of some of these reactions in the gas phase typically with an inverse of temperature. What you found out that there is really a linear fit between inverse of temperature and the natural log of the rate concept k as has been indicated by or as has been calculated from the Le Chatlier's principle. So, as that is a linear fit, you could express the two parameter here in question the x and y in the form $y = mx + c$. A question is what m and C would look like?

So, from several experimental results what you think is that if you consider x to be $1/T$ and y to be the natural log of the rate constant K, then the slope m of such a situation was also the minus change in or it was a negative of the change in p per unit redox constant R, and the intercept C in such a case, in most of the cases was also the change in entropy of this particular reaction per unit, the rate box constant R. So, these are actually experimental results and in most of these cases, in all these different equilibrium situations of different reactants and products, he obtained and uniquely similar kind of behavior where he could find out or he could generalize that for the situation, the slope and the intercept are minus H by R rate box constant minus R and delta as the change in entropy are the reaction per unit, the redox constant.

$$C = \frac{\Delta S}{R}$$

$$m = \frac{-\Delta H}{R}$$

So, also from thermodynamic if we consider this Gibbs free energy given by relationship between the enthalpy and total entropy of the system as $\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta}$. So, if we substitute for H in this particular reaction let say we want to substitute for delta H from 1. So, delta H would be also represented as $-\Delta H^{\theta} = RT\,lnK - T\Delta S^{\theta}$. So, delta H theta can be represented as $\Delta H^{\theta} = T\Delta S^{\theta} - RT\,lnK$. T delta S theta minus RTlnK. So, let say this equation is another representation of 1 and can be represented as 3. So, if we put this 3 to find out what really the delta G value would be from equation 2, then delta G theta can be represented as $\Delta G^{\theta} = T\Delta S^{\theta} - RT\,lnK - T\Delta S^{\theta}$, sorry and essentially therefore, the delta G theta can be represented as $\Delta G^{\theta} = -RT\,lnK$. So, if we consider this to be equation number 4 and try to find out if there is a relationship between nFE cell and this $RT\,lnK$ from the Van't Hoff equation, we get a very simple relationship which is the foundation for Nernst equation.

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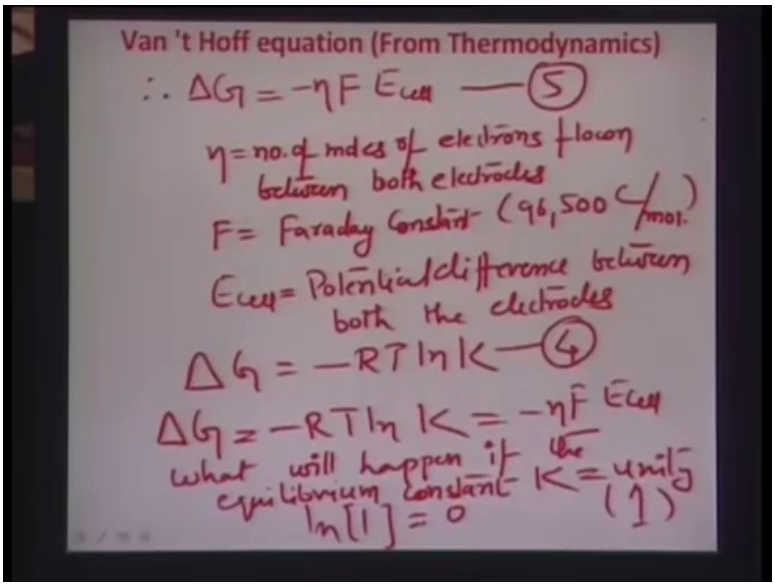

So, essentially we can say from, we can write the equation 4 again here in simpler term. So, the free energy delta G which was also earlier defined as $-nF\,E_{cell}$, where n is the number of moles of electrons flown between both electrodes and F is the faraday constant 96500 Coulomb per mole charged mole from electrons and E cells equals the potential difference between both the electrodes. So, essentially delta g also can be expressed as $-RT\,lnK$ from Van't Hoff equation, remember equation number 4. So, there for delta G which is equal to minus RT1nk can be represented as $-nF\,E_{cell}$,

$$\Delta G = -RT\,lnK = -nF\,E_{cell}$$

So here is a little problem because what will happen if the equilibrium constant K equals unity or 1, so essentially ln of 1 as we know is 0 and therefore, there won't be any free energy of the system which is available and this is a major problem which one faces. Therefore, we have to develop a strategy where we can take care of this equation, so that in the equation itself.

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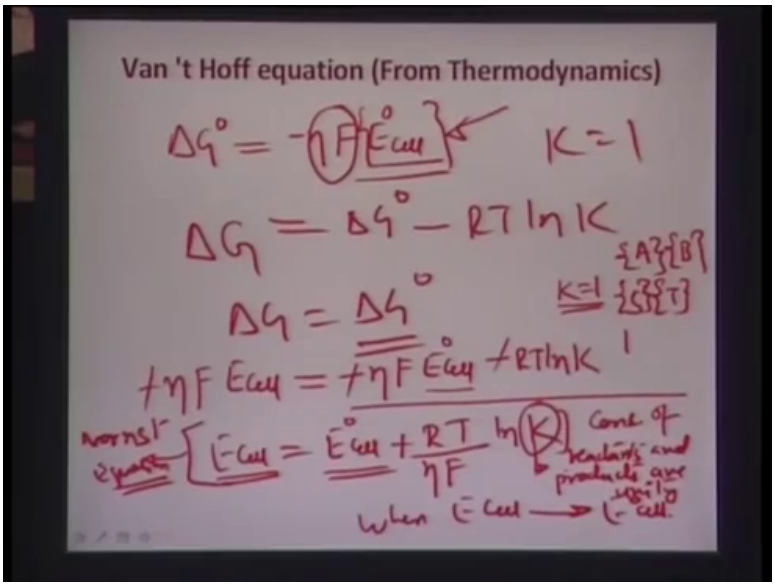

So, basically just this equation has to have you know scheme to accommodate this problem and what happens when the K value is unity. So, basically what this equation can be modified as is that let us assume that there is certain G value known as delta G^0,

$$\Delta G^O = -nF\,E_{cell}{}^O$$

where in situations when the K value becomes unity, right and then we assume that this corresponds to a value of E0 cell charge, right. So, essentially then this delta G equation gets modified to $\Delta G = \Delta G^O - RT\,lnK$.

In this case even if k is unity, the delta G value is equal to $\Delta G = \Delta G^O$ and this ΔG^O can be converted or it can be thought of as the moment of enough charges across both electrons at potential difference E^0 cell and therefore, this is essentially the final form of what we call is known as Nernst equation. So, delta G is again n and minus n F E cell from the earlier derivation, and it is equated to minus nFE^0 cell.

$$-nF\,E_{cell} = -nF\,E_{cell}{}^O - RT\,lnK$$

That means the corresponding potentials when the reactions to all one molar in concentration,

k mind you comes equal to 1 and one of the cases that when all these different activities that we have been in considering of K B S and T comes out to be equal to all unity.

So, essentially you know nfE cell minus n of E cell can be equated to minus nFE naught cell minus RTl ln K and this is what final form of Nernst equation will look like. So, we can calculate the E cell value by just looking at E naught cell and this term here RT by nF ln of K. E naught cell again is the cell potential in all the concentrations of so-called reactants and products are unity when E cell becomes E naught cell. So, that is essentially what the Nernst equation is all about. So, now, it is a very interesting thing that comes out that you can really equate EMF the potential of such system to the concentration of the reactants and products that is again whatever goal is in all sense that if analytes or analytes of interests are detected by looking at the EMF values of the particular cell.

$$E_{cell} = E_{cell}^{O} + \frac{RT}{nF} lnK$$

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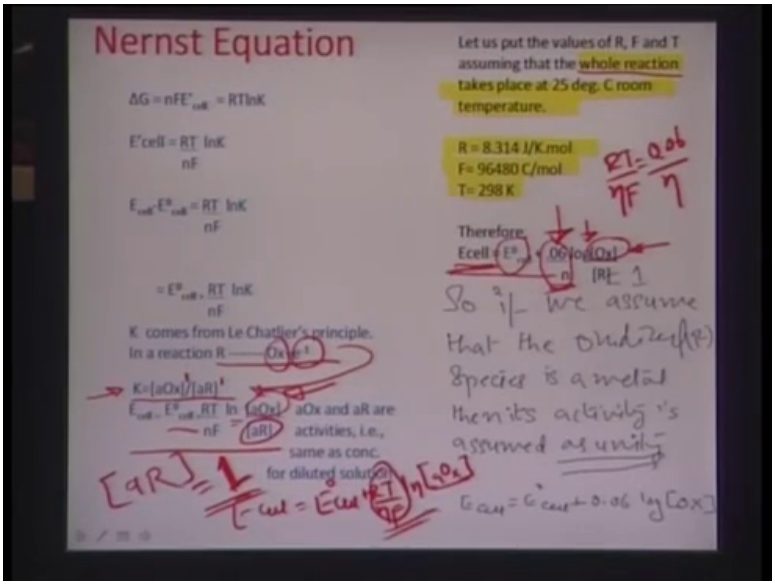

So, let us do a little bit of a post calculation on to this equation. You know there are two aspects which I would like to mention here. One is, let us think that in a reaction, a certain reactant R is getting converted oxidizing into species ox again giving in electron, right. So, in such a reaction, the rate of reaction can be written as the activity of Ox to the power of stoichiometric co-efficient which is 1 in the case divided by activity of r, the material that is getting oxidized to the power of its own stoichiometric co-efficient which is 1 in this case. So, therefore, K can be written down as the activity Ox by activity R. In case of EMF if you look at EMF E cell and Nernst equation, it comes out to be E0 cell by this equation plus r t by

n f natural log of k, and k is activity of Ox by activity of R and essentially when you are considering case where there is a metal electrode and its corresponding salt solution, we can safely assume the activity of the metal as unity because it does not have its own ionic state in the solution in case, it is fixed and it gives ions though and those ions have a certain activity aO_x .

So, in that case Nernst equation can change to e cell equal to $E_{cell} = E_{cell}^{O} + \frac{RT}{nF} \ln\left[aO_x\right]$

because R is unique. In this case let us also look at if we can do something about this $\frac{RT}{nF}$.

If we assume that the whole reaction takes place at a room temperature and standard conditions, it is 25 degree Celsius and if we take the value of R to be 8.34 joule per Kelvin mole, the value of F, faraday constant is 96480 coulomb per mole, and t of 25 degree Celsius means 298 Kelvin. Therefore, we can calculate $\frac{RT}{nF}$ as 0.06 by n. So, therefore, in the Nernst slope of the E cell really comes out to be 0.06 by n. So, if you plot the E cell with the logarithm of the oxidant, the concentration of the ion which is also propositional to the concentration of analyte to interest is the cases where analyte is getting oxidized, and then the E cell and the concentration are really in the terms of linear equation. That is a beauty that the slope of that equation is also inversely propositional to the number of moles charge transfer that is taking place and the intercept of that equation is essentially is E0 cell.

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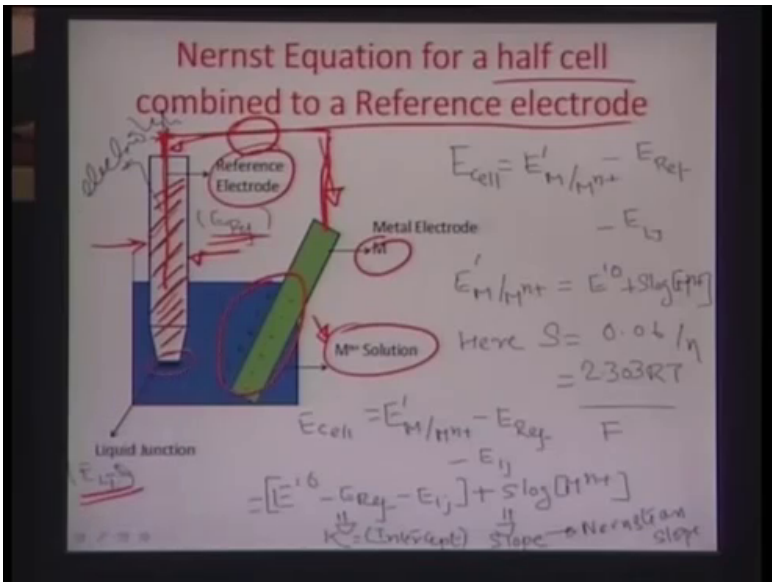

$$M/M^{\square}\ E^{'0}+S\log\frac{n+M^{\square}}{E_{\square}}$$

$$S=\frac{0.06}{n}=\frac{2.303\,RT}{F}$$

$$M/M^{\square}\ E_{cell}=E_{\square}=E_{ref}-E_{1j}$$

$$M/M^{\square}\ E_{ref}-E_{1j}=\left[E^{'0}-E_{ref}-E_{1j}\right]+S\log\frac{n+M^{\square}}{E_{cell}=E_{\square}}$$

So, let us now look at some practical electro design problems and from this essentially we will move on to the corresponding MEMS modules of electrodes which would essentially use the same principles of electro chemistry, but then they will have to be considered on because of the initialized size, there have to be the other aspects like an ionic strength or the concentration of ion of interest or whether there are ant completing ions in that, such a solution which formulates in major, the major paradigm for designing such electrons. So, let us look at this half-cell combined to a reference electron. Let us look at the drawing here to begin with. So, you have some kind of a reference electro with respect to which we would like to measure the interaction between the metal getting in two solutions as an oxidized metal m n plus. The reference electrode here is essentially nothing but a glass capillary which is covered by this liquid junction and this develop potential let us assume E_{1j} with respect to the solution, and inside this glass capillary, we have this electrolyte which is a very standardized and it has a standard concentration and it has a sensing reference electrode here which goes in to the electrolyte.

So, any charge transfer that is taking places thorough this liquid junction and through the electrolyte which is inside the capillary, and then goes on to this conduit as why are here you can see and this essentially formulate and EMF here because of this configuration and can be in the reference electrode with respect to which you measure in the activity of a metal and a solution like this. So, if we look at if we really connect these two you know externally, let say we are trying to measure by connecting these two externally using Volt meter. Give me one minute.

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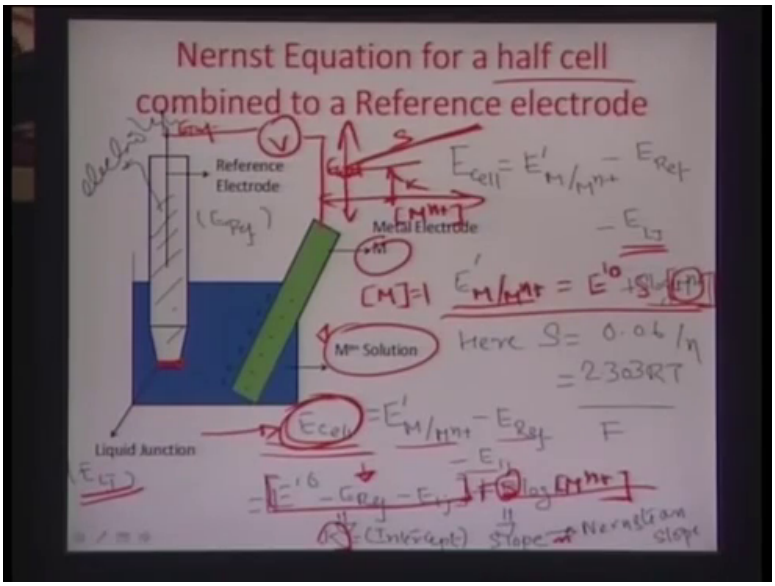

So, let say we are just trying to connect these two electrodes externally using voltage measuring device. So, in that case the E cell in this particular configuration can be written down as the E dash metal to metallic ion inversion M to M n plus conversion $E'_{M/M^{n+}}$. So, the potential of this interaction between metal and the metal solution or the salt solution of the metal minus in the e reference potential which is at this point E_{ref} minus again the liquid junction potential which is again contributing to the ion exchange process between the external solution and the internal solution. From the Nernst equation as we know already if we consider the activity of the metal here to be equal to unity E dash cell in that case, E' of this oxidation of EMF produced by the oxidation reaction can be written down as the E'^{0} the oxidation reaction corresponding to the case when the reaction rate is unity or the rate constant k is unity plus the Nernst slope plus 0.06/n log of M^{n+} the concentration of the oxidant, and essentially so the E cell can be represented as this particular value here which is $E'^{0}+S\log\frac{n+M^{\square}}{}$ oxidant minus c reference minus E_{1j}.

So, we can actually pull this together make this under the same bracket as $\left[E'^{0}-E_{ref}-E_{1j}\right]+S\log\frac{n+M^{\square}}{}$ and this is essentially a straight line. So, if you plot the e cell value here, give me one minute. So, if you plot the E cell value, let say we plot it here with respect

to the concentration of the oxidant m n plus, right you get a straight line from this particular equation. Why which is e cell equal to m x n being the slope s plus c which is $E^{'0} - E_{ref} - E_{1j}$ resume this to be scale suppose and this to be slope m. So, this here is really what this slope K is of the intercept K is and the slope of the straight line is s. So, therefore again this EMF of concentration is strange in hierarchy, alright.

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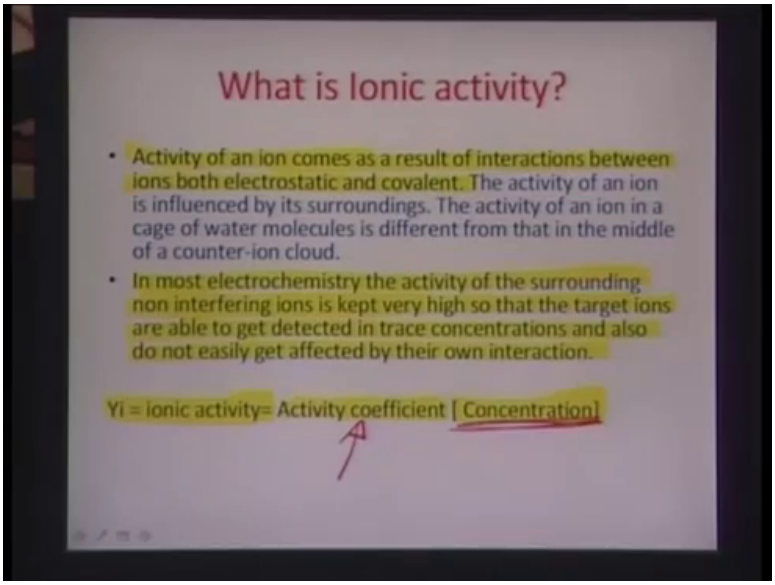

So, the next point which have I would like to emphasize is that really if you look at this solution on a very close bases, there is a lot of other activity which is going on inside the solution and the concentration of ion is really very diffused because there are so many other ion to ion attraction and interactions which are happening that really can we say that the ion of interest that we are looking at has exactly the same effect in the charge transfer process as its concentration. So, therefore, it is pertinent to describe term which can give idea of what happens when these small ions is interacting several other competing ions. There are forces of attraction, there is repulsion, there is you know change in over all state, there are so many counter ions which are there in this solution, let us say we are detecting calcium plus 2 positive calcium ion. So, there are lots of let say ions around it is. So, these are counter ions. So, there are ion clouds and there are, this you know just central ion of interest. So, the activity of an ion is the corresponding you know the corresponding factor, the corresponding term which can give an idea of the interaction between ion port electrostatic and covariant.

So, the ionic activity can be defined as often ion can be defined as the result of the interactions between ions, both electrostatic and covalent and the activity of an ion is

influenced by its surroundings. So, if suppose ion is in a cage of water molecules, it has many different activity factors than when it is in a middle of the counter ion-cloud. The most electro chemistry in the activity of the surrounding non-interfering ions is kept very high, so that the target ions are able to get detected in trace concentrations and also, do not easily get effected by the own interactions. So, this is something very critical to be observe that inspections where you have several completing ions, the best way to reduce the interaction between this completing ion is to create a high ironing background and essentially you create something, some ions are something which is having the ion exited, but it as non interfering with ions of interest. So, if such a kind of situation happens when you can by and large create a huge background, so that these interactions between the competing ions become very small or insignificant.

In that case the ionic activity which is more appropriate time given an idea the electronic interactions can be described is a activity coefficient and this is a constant terms the concentration of that particular ion. This activity coefficient can be you now in different situations, it can have different values where sometimes ionic activity can be too high and sometimes it can be too low, and the idea is if you have a surrounding non interfering heavy ion-cloud around the target ion, it kind of gets equal to the concentration at the ion and you can easily get to detect the exact quantity of the target ion of interest. So, therefore, an especially in MEMS kind of protocols and other we are talking about selecting over a very small you know very small volume of liquid. There is always almost always a tendency of the activity to be very much different than the concentration. So, so we are next going to find out how it is possible by designing electrode to pick up a certain ion over let say several competing ions and that is how we get into the field of ion selective electrode.

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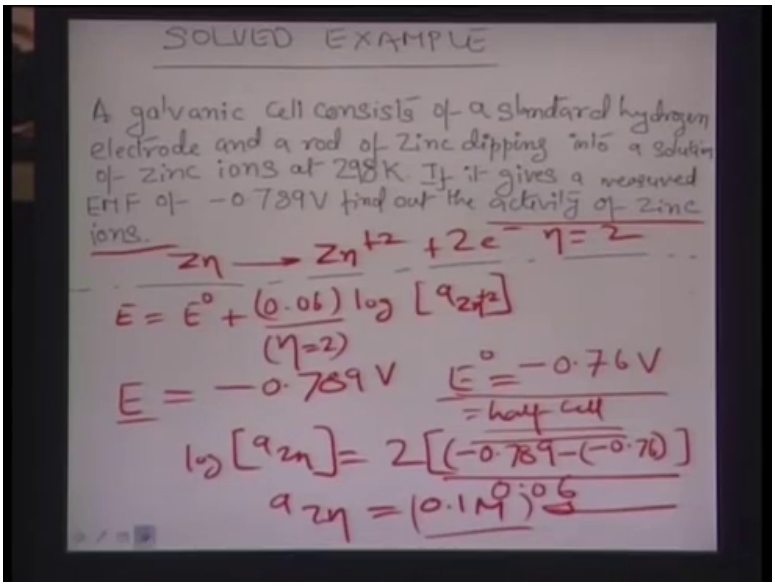

$$Zn \rightarrow Zn^{+2} + 2e^{-}$$

$$E = E^{0} + \frac{0.06}{n=2} \log\left[a_{Zn^{+2}}\right]$$

So, basically let us do a little bit small problem on finding out EMF before going to the ion selective electrodes. So, in this example there is an organic self which consist of standard hydrogen electron and a rod of zinc dipping into a solution zinc ion at a 298 Kelvin and if it gives the measure d m f of minus 0.789 volts, find out the activity of the zinc ions. So, we apply the Nernst equation here and essentially the e cell this case can be represented as the E 0 cell plus the Nernst slope 0.06 divided by n. N in this case because it is zinc carrying oxidized into and zn and plus two electrons and n is actually two in this case, and into log of the activity of zinc plus two ions. So, it is good I mean it is given in the problem that the EMF e of this particular cell is minus 0.789 volts and you know this with respect to a standard hydrogen electron. So, the E zero the standard potential with respect that electrode from the tables which I have described in my earlier lectures comes out to be 0.76 volts.

So, this is essentially the half cell potential. If you remember we have discussed a table where all these in half cell potentials were found out by connecting the respective cell to a standard hydrogen electrode. So, from this equation therefore substituting the values of E and E zero and n equal to 2, we obtained the log of the activity of zn as two times of minus 0.789 minus of minus 0.76 divided by 0.06. The activity of zinc comes out to be equal to 0.1. So, so the activity of the zinc in this particular example is around 0.1 moles. It may happen the

concentration of the zinc happens to be more due to the shielding effect activity may be little less.

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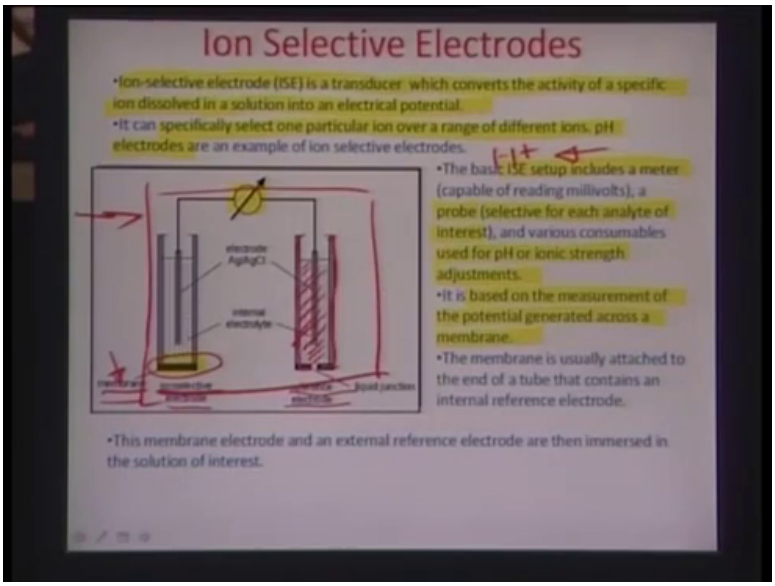

So, now let us look at what these ion selective electrodes are or what they do. So, we are very often faced with the problem of deduction where there are more than one compelling ions in a particular solution and in that case we want to find out a particular ion in analyte of interest. So, essentially the ion selective electrode is transducer which converts the activity of a specific ion of interest dissolved in the solution into an electric potential. So, even though there are more than one such ion in the solution and the ion of interest has to be specifically reported using ion selective electrode. So, if the basics set of ions let us selective electrode can be at represented here in this particular figure and if you look at the set up you can see that there are two electrodes.

One is the reference electrode which is made in a similar manner with the capillary and essentially have good junction like any reference electrode would make, and electrode immersed inside a solution of standard or known concentration of ions and the ion selective electrode essentially is a kind of copy of the same with an exception that instead of the liquid junction, you now have a membrane here which is selective to ion of interest. So, therefore, this membrane is designed in a manner there it can take up only a few ions of interest from this solution which this membrane is designed to take up. Therefore, this whole assembly is immersed inside the analyte of an interest and the potential a of is found out dif potential difference, found of between the reference and ion selective electrode.

So, therefore, we can say that it can specifically the job is to specifically select one particular ion over a range of different ions. For example, ph electrodes and just picking up hydrogenates. So, the ph electrodes picks up only hydrogenates and leaves the other once behind. So, therefore, that is an ion selective electrode. So, the basic IAS set up includes the meter, prob-selective to each analyte and the selection is done by using this small membrane here, and essentially it also uses various use for pH and its strength adjustments. This is important because you want to create a large background of ions, so that you can pick up and ion of interest in that background. So, the interaction of that particular ion of interest with other ions surrounding it are eliminated by the strong interaction forces offered by the background in general, but again as a background ions are non-interfering in nature, they would really not contribute to any charge transfer process. Only the charge transfer would come due to the particular ion of interest.

So, an ion selective electrode is essentially is based on the measurement of the potential generated across a membrane here, a selective membrane here. Membrane is usually attached to the end of this tube and essentially there is a solution here for internal reference of this particular electrode and the whole assembly is immersed to the analyte for the measure purpose.

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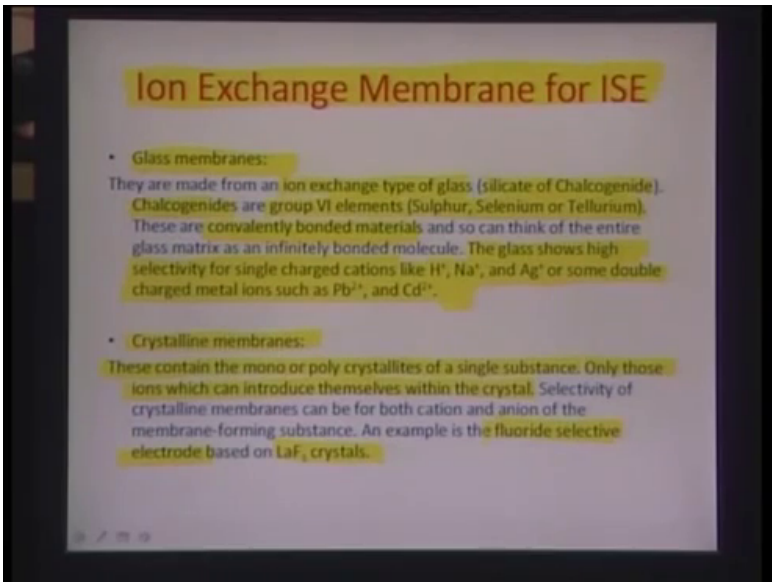

Let us talk a little bit more about what these membranes are or what they are supposed to do. So, the basic property that is important on to the ion selective electrode is by virtue of the membrane. So, the membrane should have some characteristic or some feature may be if a network of pores which might match to certain ion sides, it might be able to pick up certain

ion over n number of other competing interfering ions. So, there is a size base selection in that case. It could be also made up of some biological material which can recognize only a certain ion or a certain group of ions of interest. So, essentially there are several different kinds of ion exchange membranes that are available for designing and selecting electrodes. Let us look at these one by one.

So, there are these glassy membranes which are made from you know an ion exchange type of glass and they are typically the silicates of Chalcogenides ion metals. Chalcogenides if you just recall from in the group 6 of the periodic table as sulfur selenium tellurium. These are Chalcogenides, the group 6 of the periodic table. So, essentially the silicates of such metals form excellent time exchange type of glass materials. So, they are covalently bonded materials. So, you can think of the entire glass matrix as an infinite bonded molecule. So, it is one bonded molecule with in between spurs of these sulfur, selenium, tellurium these kind of metals. So, such glasses have the tendency by may be the virtual repulsive structure is to show to show high selectivity for single charged catioms, ok. So, I am slight let say hydrogen plus sodium na plus silver or some at the most some double charged metals ions, such as let say lead and cadmium ions. So, these classes shows tendency of just hearing to certain size with the single charge and certain size with double charge. That is why it is related something to do with the crystal structure of this covalently bonded of silicates of hydrogenate ions.

The other types of ion exchange membranes are crystalline membranes. One example that I can code is the lantana fluoride crystals of fluorine ion. So, essentially this is the size base selection again. So, this contains mono or poly crystallites of single substance and those ions which can introduce themselves within the crystals are selected by virtue of the membrane informed by this specialized material. So, these are some of the various types of ion exchange membranes that are available.

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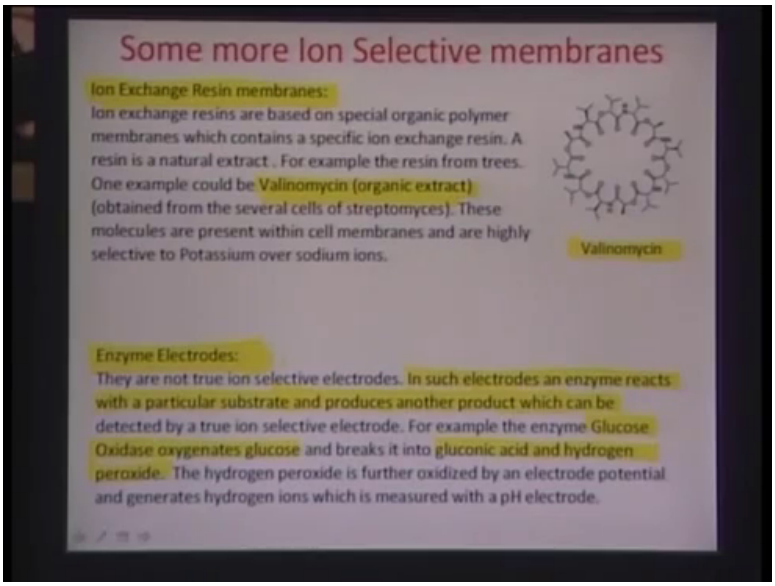

Some more could be these ion exchange resent membrane. These are very interesting in nature. So, there is a compound called Valinomycin. This is normally available in the cell membranes of Streptomyces and essentially the purpose of such a compound is to give way to the processes of exchange of potassium and calcium ions between the periplasm and the cytoplasm of certain cell. So, therefore, if such kind of materials can be again enclose and encrypt inside polymeric material or the polymeric resin, it can form an excellent source of selection of potassium or calcium just as it happens naturally in case of cell by virtue of opening and closing of ion channels inside you know the artificial membrane that you make using these.

So, the whole idea here is that valinomycin which is also an organic extract, especially it is you know it is a natural extract you can say can be used to form the same application that it is used for naturally. This can be a fantastic answer to an electrode. Other type of ion exchange membrane is really enzyme electrodes, although these are really more related to the overall selectivity of an analyte of interest. So, what happens that in such an electrode there is enzyme which would react to all the particular substrate. So, the whole purpose of sensing or detection is to detect one particular species over the other competing species, right. So, in this case the particular enzyme may just react to the species of interest say for example, Glucose oxidase I have mentioned earlier n number of times. This glucose oxidase enzyme would odxiate glucose and breaking into Gluconic acid and hydrogen peroxide. Therefore, this is again giving a selectivity aspect to sensing mechanism where one peroxides can be measured by pH electrode which has some other ion selective membrane which can be some places

which can easily take up the hydrogen plus ions over the other competing ions.

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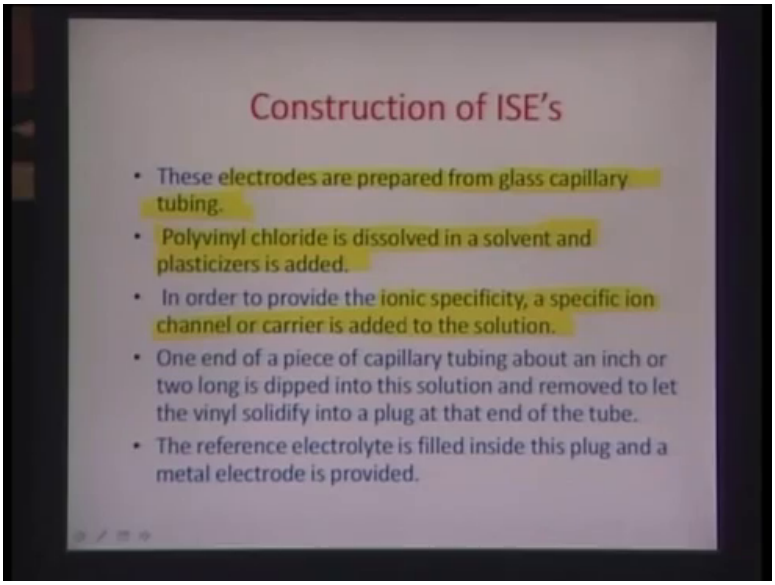

So, there are most cells what an unselected electrodes and how they are constructed. So, essentially the electrodes are prepared from glass capillary tubing and there is a material in most of this polyvinyl chloride BVC which is dissolved in a solvent and added some plasticizers. I just like to recall the plasticizers give this unique ability of the polymer to flow more you know by getting into a change of a polymer and make a change role over easily. So, you add some plasticizers from making it more fluidic in nature especially when they are in the liquid form before they cure. So, therefore, this particular ion specific material whatever you have to design is added to this particular solution and then dips in the capillary solution and solution gets into the end and forms small plug, and then plug is provided certain and you know certain strength, ionic strength of a particular solution is put into the glass capillary. Therefore, you have this capillary, the solution sided conduit which is coming out and then, the end which is the plug with maybe polyvinyl chloride polymeric resin with an ion exchange material trapped inside it. So, this can give properties of what ion selective electrodes would essentially need. The reference electrolyte which is filled inside can vary depending on what analyte of interest is being measured used in this particular electrode.

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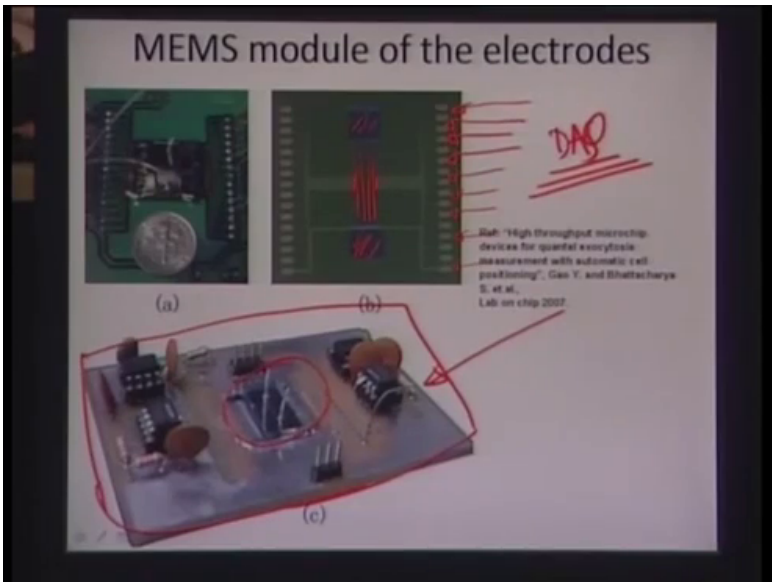

So, when we talk about the various MEMS modules for electrodes, you know the basic idea of MEMS is that whatever is being done by the conduit be transferred on to a micro chip level, and some of these electrodes essentially can be you know screen printed on to these chips rather than just you know hanging plain wires. Say for an example if you look at this particular chip here and this is again you know lab on check as a paper put in lab or measurement of exocytosis processes you know in single cells essentially and this is also in a set of work that had been earlier done in our group. So, if you see here these are screen printed electrodes on a silicon wafer which can be easily fabricated using this micro fabrication strategies that we have been talking about before, and there are these in this small positioning channels, this narrow small positioning channels between these sensing electrodes and two reserve wires essentially on both sides here.

So, there is a flow of cells and positioning of cells over these individual channels or electrodes and ion exchange resin here can be coated spin coded selectively lithography certain specific areas, where these electrodes interact with the solution of interest and can be rapidly recorded using a DAC system (Data Acquisition System). So, all the electronics can be built surrounding the particular chip here of interest and this can be a BIO MEMS device to measure electro chemistry of a single cell.

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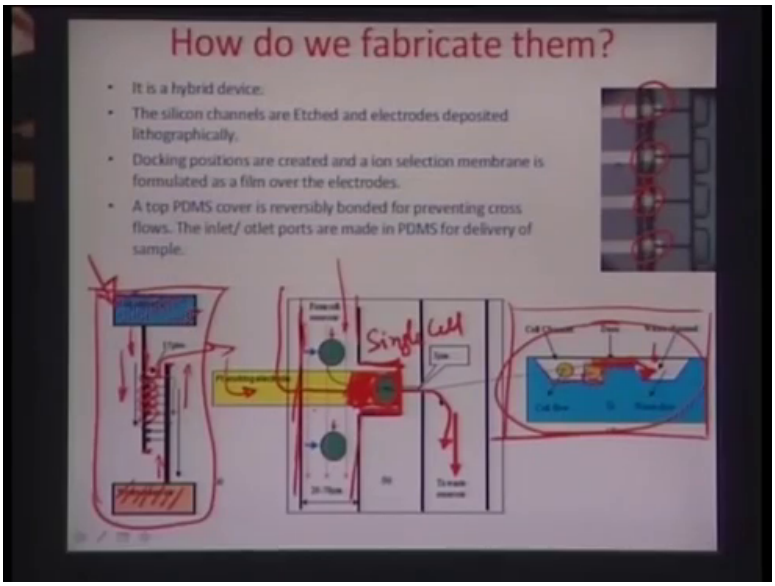

So, how do we fabricate some of these devices to make the positioning of the cell is very interesting, that you basically make a channel here in this particular form in a silicon in a manner that is shown like this. So, this essentially is the top evaluation of the device. So, you have cell reservoir on one side. These are all microscopic features and you have transportation channel which is locked here at this particular end. So, this channel is locked in one end and immolating out of this cell reservoir, and there are these docking stations this in small 15 microns by 15 micron docking stations which can dock a cell like this. Following this there is a small channel, very small channel which is lower than the size of the cell, but can essentially flow the fluid which is scarring or stopping transporting cell to this docking station.

So, if you look at this whole assay on the side view, this is essentially where the cell would go and dock, right and this is the small dam which is able to connect both sides. That means side 1 and side 2 on this device. So, this is the waste channel side. The waste channel side is similarly positioned. So, if you see the waste way side, you find out that the waste side also has a channel eliminating from this waste reservoir and it goes on stops are get blocked all the way here and there are connecting channels in between the main flow channel and the waste channel in this particular manner. So, the cell comes here, docks itself and the solution which carries the cell is able to move from this particular dam area into the waste area. That way the fluidics is made continuous, the fluid flows made continuous. So, the fluid comes like this, goes into this area because it cannot go ahead anymore because it is locked in here. There is a certain pressure here and it comes and positions the cell and moves out into the

ways the reservoir something like this, but then we can actually make the docking station of the size of single cell.

So, therefore, if it is 15 by 15 microns and we assume the diameter of this particular millions cell is above 15 microns, this is what happens. You have these cells here kind of dock in these docking stations and the electrodes, the platinum working electrodes are placed just about the docking position and here, you can keep the ion exchange zinc in form of a coating, so that whatever happens to the cell or whatever happens from the cell through sign channels can be easily gauged using this platinum electrodes through this ion exchange coatings which can be given on the membrane or which can be given on the top of the electrode here. So, this is a fantastic example of how an electro chemical device can be fabricated from MEMS platform to motivate MEMS platform.

Thank you.