

**BioMEMS and Microfluidics**  
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**Lecture - 08**

So, this actually is a review of lecture 4 to 6. Last week we had actually talked about some introductory concepts of BioMEMS and Microfluidics. This week we were more focused to a transduction and we started actually with soft lithography and describing various fabrication techniques available for polymers which include replication and molding process, depend lithography, micro contact printing, micro molding in capillaries, solve into system molding so on and so forth. We talked in great details about nano imprint lithography which is a compression molding process. Compression molding as we all know is a process by which is a hard substrate which does not vary much with respect to changes in temperature and pressure is used to apply squeezing pressure on to the top of a thermosetting plastic material and the plastic takes a negative shape of whatever imprints are available on the surface of this mould, and then the mold is removed.

So, we also saw how this process is modified slightly at nano scale where we use a shadow masking by PMMA and deposition approach of metals followed by using those metal pillars of post printed at the nano scale resolution into another polymer which is like a thermosetting polymer. We also discussed how this process is very important for the semi conduct industry. We talked in great details about transduction processes where we actually where concerned with electrochemical transduction, mostly discuss concepts from potentiometry which is basically the measurement of cell potential and zero current and the potential varies as a function of the concentration of the analytic of interest. We discussed in detail Voltammety which is some kind of a voltage sweep technique which results in the reduction are oxidation of different species which are present the solution.

So, this generates and idea above what the species are as well as concentration the species are looking at the potential corresponding to the peak in the curve as well as the height of the peak. We get this process identically repeated for the oxidizing or to reducing species and typically that is wherever that redox couple we like to use the technique. We also talked about Conductometry, where there would be a cell which is created and the conductivity of the solution varies and the cell formulates one of the resistance as in a Wheatstone bridge arrangement and as conductivities variant, we can easily detect the concentration based variation of the conductivity by looking at the bridge balance. We talked in great details about

basic cells, half cells and electrodes just sort of a (allow me recall) how we started when we looked into a piece of zinc dipped in a solution and how do a layer would come into existence. So, we typically looked into metallic structure, the metallic bond which is nothing, but sea of electrons going around positive charged centers, and we further went into how the brown in motion of the interfacing fluid would result in movement of few ions into solutions which would be a irreversible process because the movement the ion is introduced to the solution, there is a tendency of the ion to get hydrolyzed, and there is a water mono layer we should prevent this ion coming back into the electron.

So, there is always a separation and insulating separation between this array of ions formulated just close to the electrode in a solution as well as the electrodes which is left over on this because of this ionic release. So, we talked at great length about how this process can continue if there is a redox couple which we put in and discussed various properties of this small layer we should be asked a small as a few atomic diameters mostly about probably less than nanometer, a tons of nanometers and we also discussed about the tons electric field of the order of millions of holes per meter which is available in this in a small layer and the redox couple if introduced by looking at two species, where one of them be able to displace the other from it salt solution being placed in the electro activity series would tend to continue this process for a longer time, thus resulting in a deposition of metallic substance on the top of this process.

We particularly discussed the case of the zinc in copper sulphate solution, where there would be a brownish layer of copper deposited on the top of the zinc surface and it would be a self starting process. We further assume that if what would happen we want this process to continue a little bit further by looking at what is called electro, by looking at a electrochemical half cell which would typically be one of the electrodes dipped in its salt solution and two such cells together, connected together through to an external wiring making an external circuit. So, we talked about the example that we provided in this was a Daniel cell, where one of the electrodes would be made of zinc dipped in its salt solution. So, another electrode would be made of a copper dipped in its salt solution. So, the idea in such a cell is that while one of the species get oxidized in the solution also known as anode, and we look at this from a stand point of the solution that anode is always the species which gets oxidized by providing positive charge into the electrolyte or solution, and the other species which actually is able to displace the ionic metal from its salt solution. So, in this particular example in the Daniel cell, you have copper and copper sulphate. So, this copper sulphate has

the metal in the ionic state as plus 2 oxidation number. So, Cu is present as Cu plus 2 and the mechanism is such that Cu plus 2 is able to get this place from the solution and gets deposited back on to the electrode. So, in a way it is a cathode because when we are externally connecting the anode which generates the electrons externally or in the external circuit, electrons typically go and into the copper side which is the cathode and these electrons are utilized for changing the oxidation state of the metallic copper which is deposited on the top of the electrode by virtue of this electronic such process.

So, in one sense in such convention we assume that the electrode with sense in positive charge in the solution is the anode, and on the other side because of this deposition process we can say that in an equivalent manner we are creating a species in the solution. For example, let say in the copper sulphate case, as copper displaces from copper plus 2 from the solution state and gets deposited by technique electrode from the copper electrode on the top of the electrode itself, it creates cell of  $SO_4^{-2}$  in the process. So, therefore, we can say that this just action of deposition of the  $Cu^{+2}$  uses to state is creating or liberating negative charge. So, therefore it is treated as a cathode. So, we looked into the sign convention which is internationally nationally available for looking at both the electrode, that is one of metals in the salt solution and similarly the other metal which is the cathode sits in its own salt solution.

Then, we short of made relationship that the way that we choose the metals is on the basis of what is going to displace what from its sort. For example, this purpose we look into the electro activity series where zinc is placed much higher in terms of its ability to displace hydrogen from steam or acid or water in comparison to copper. So, copper definitely is the species which would get displaced from its salt solution and zinc is added to let say copper sulphate. So, in a way it is about estimating what is good redox couple. We should be needed knowledge wise to formulate these two half cells. So, once the half cell is designed, we try to find out the potential between different electrodes of this half cell, and here I would like to recall that we discussed not only the metal solution interface but also, case where we had the solution of two different oxidation states. For example, the ferric and the ferrous state and there in such kind of example we always saw the participation, the increase participation from inert species to carry the charges, such transport from one side of the half cell to the other side of the half cell. In that particular case, we used platinum if you may recall.

We also talked about some other form of electrodes like gas electrodes or salt electrodes,

where particularly we would use species which is not dissolvable in water like particularly we mentioned the case of using silver chloride as an electrode. We further estimated the cell potentials by looking at different mole ratios for reaction which would have different oxidation states participating between particularly the oxidation in the reduction reactions. We also tried to estimate the concentration by looking at the potentials and came into the derivation, the complete derivation from electrochemical theory of the Nernst equation, where we used the free energy of a particular cell and equated that to the energy that would be needed in transporting  $n$  moles of charge from one side of the half cell to the other, and we could actually correlate this  $\Delta G$  and free energy to the Van't Hoff equation through which we could cut the equilibrium constant  $k$ .

We also discussed in detail about ion activity. The activity maybe different then the ionic concentration because naturally in a environment of all different kind of ionic species, the activity of one particular species and by activity I mean to say the electrochemical activity would get jeopardize because of the several columbic interaction which are happening which is system by another species. Therefore, concentration may not be exactly reflective of the ion activity. We in fact talked about finding out an activity coefficient which is the factor which could have to be considered for getting a relationship between the electrochemical activities of ion on one side concentration in the solution that we are trying to measure. We briefly discussed about ion select electrodes, particularly the agents or the materials which are available to make such ion exchange membranes which would be contributing towards formulating the ion selective electrode.

Typically, will looked into an architecture which will be made out of let say a polymer like previously we should be porous and also be able to trap some of these materials which are selected in terms of their different ionic species of particular elements are the glass membranes where we talked about chalcogenide, and we also talked about their ability to show high selectivity for single cation like hydrogen, sodium, silver so and so forth. We also described about crystalline membranes particularly the lanthanum fluoride membranes which should be highly sensitive to fluorine ions. We further discussed some very unique natural materials which are available because of the processes that mother nature by self or by herself executes in cells and in that context we mentioned about Velinomycin which is actually an organic extract obtained from several cells of the streptomysis and this is a material which is abundantly present in cell remembrance to have high selectivity over potassium over sodium ions, and such material can often be extracted and used for the purpose of ion adding, ion

selectivity to measurement system in a electrode.

We also discussed about enzyme electrodes particularly in case like that of glucose detection, where it could be very relevant to use an enzyme giving recognition component to the analyte of interest over the several other species which are available in a solution. So, we discussed about the construction of how IAC can be formulated by using polyvinyl chloride, trying to end cap glass pipette where there would be the presence of a wire which could do the electron transfer and typically look like half-cell, electrochemical half-cell. We then discussed in details about the various aspects, practical aspect to formulate ion selective electrodes where a majority of studies would indicate the solution preparation of the solution designed as the biggest challenge for realizing ion selective electrodes.

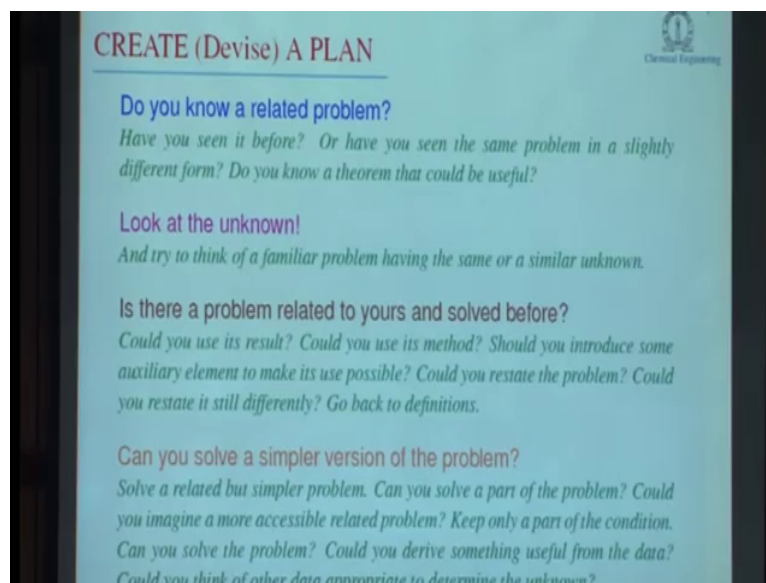
We also dumped into the measurement calibration of such electrodes, where we used three different methods for doing the calibration. The first method would be the direct reading method and there would be 3-4 known concentration verses EMF characteristics which are already available and we tried to generate a plot of EMF with lot of concentration, and then whatever would be an intermediate concentration between the steps would be read from that calibration graph that would have been issued a plot for any particular electrode. We also talked about some other methods like standard addition in grand plot method, where in one of the standard addition methods, the known amount of standard or higher concentration sample usually about ten times the concentration, the expected sample concentration is added and before addition and immediately after addition, a voltage measurement is made which would be the bases of calibrating in the particular electrode. In this context we also did some numerical design of how such electrodes can be calibrated with that method. In the grand plot case, we would extend the single standard addition method into multiple additions and try to again formulate plot based on  $10 \log$  of EMF on one side on the y axis and the standard concentration on the other axis and then, extension of the standard concentration would provide an idea about the unknown concentration which is present in a solution. So, instead of a single addition as in the standard addition case, in the grand plot case we do multiple additions which give us higher efficacy or I would say higher accuracy to read out of the electrochemical potential.

So, two things that sensor designer particularly in electrochemical transduction needs to necessitate are number 1, you have to design the solution very carefully and number 2, when you are talking about the calibration processes, the moment you have more number of reference electrodes and more number of calibrations like additions of solutions etcetera like

in the grand plot, the accuracy of the read outs that eventually result would improve because of that. So, therefore, these techniques are very commonly used for the electrodes that you obtain for the sensor design. The idea then would be that how you can miniaturize electrode and take it to a scale where you can do, these are the micro scale where the relevance to the BioMEMS and Microfluidics would come, and in short I am going to talk this over in the next few lectures to come.

Thank you.

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Once I passes generated, then how we analyze, but the first idea is not coming to you, and many of these things triggers for really wonderfully well. You know related problem like terminal. I will give you some example. Terminal velocity means in engineering we think falling. So, that will trigger the physical process there and those physical processes you try to apply to your problem. Then, look at the unknown content, just looking at the unknown tells you some time you need some time unique different like this. May be that will apply.

Another beautiful one is either a problem related to yourself called before. This is what called research, in engineering research. You know you look around if somebody done something similar and then they give you ideas. This of course applies what is already known to you, but still looking for it in the net, in the journals whatever it is done. Now, these are really wonderful one. Can you solve a simpler version of the problem? I recover to whole heartedly really wonderful one if problem is too complex, can something done? Solve a simpler one. When you solve the simpler one, you get an idea how you can attack more complex one. I

have done this so many times myself. So, many times we try to do something very complex, then say forget this complexity. Do something different and may make a problem simpler and the simpler problem when you solve, you get an idea of how you can solve the more complex problem, and these are very beautiful triggers and they work very well.

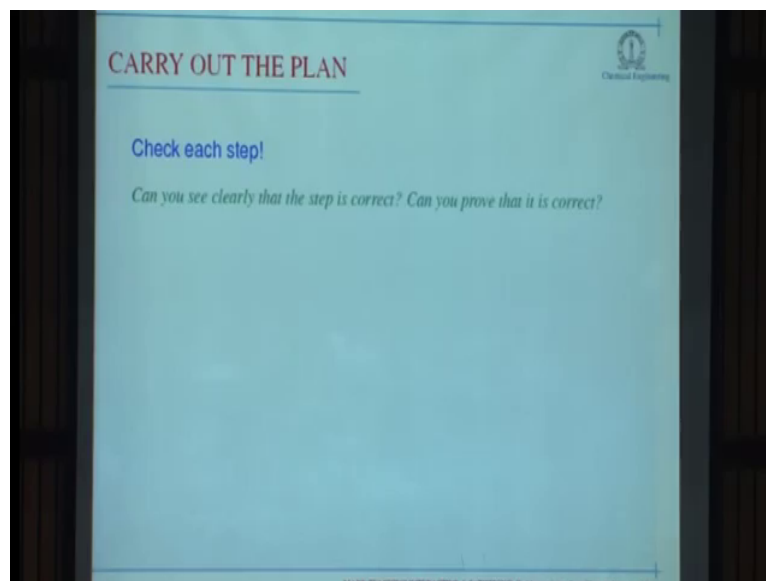
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So, that is these things when you look at those sentences, these are what is meant by trigger. When you go through a systematic manner one by one, then one of it will work for you. I mean is not a guarantee, but this is what triggers are supposed to do.

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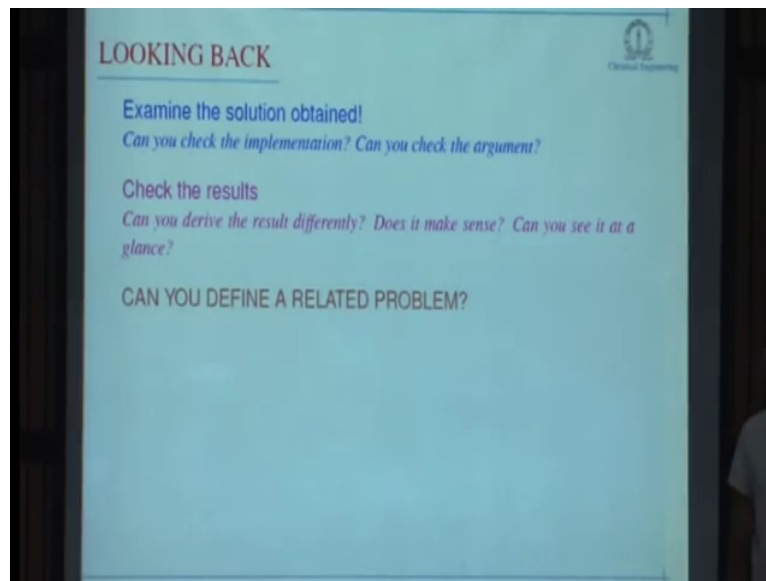
Anytime you have any question please ask me. You do not have to wait here. I am always happy when you ask a question.

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I am not going to emphasize this because it is not my interest that I think people teach the whole of books read how to do things. I am not going to emphasize on that. You must of course start to make silly mistakes. Do not add 1 plus 1 to 4. That will be wrong of course. So, you must take all that but there are many books which wrote about that, so I won't emphasize that.

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Now, this is one thing really very good. I recommend this whole hearted to all of you. Looking back, examine the solution obtained. Is it making sense? When you throw a ball, it is coming down and going up? Final velocity is right or wrong? So, when viscose is going or things are moving fast or slow, when you increase the pressure what is happening? So, you internalize the solution that is what is meant by developing intuition for solving the next problem. So, you own the knowledge. You will now be able to tell why something should happen. I think one of the cases where it now, by memory is terrible. I cannot remember the name. He said that you how understood the problem, then you can predict what the results are when you have the equation.