Bio-electrochemistry
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Lecture – 16
Types of Electrodes

Welcome back to the lecture series in Bio electrochemistry. So, we are into the fourth week and we are starting the first lecture of the fourth week. So, if you recollect, the last lecture was about a concentration cells, we talked about it, how you can translate the Nernst equation for the biological cells.

So, today what we will do, will go one step ahead. Now we will talk about some of the electrodes, and relevant potentiometry. So, when we talk about potentiometry the word which evokes in your mind is a potential anything to do with potential potential means voltage. So, there are 2 parameters, when you look at ohms law V is equal to IR, it is essentially potential difference, potential V is equal to I which is the current and resistance.

So, there are only 2 parameters which you can vary or you can measure, either you measure the potential or you measure the current, when we measure the voltage or a potential everything falls under potentiometry, when we measure the current they fall under amperometry or current measurements different electro set of electro nautical techniques. So, at this point what we are talking about if you look at we are always talking about potential like E 0, E.

So, all the measurements are about potential, we are not talking about the current measurement. So, in terms of the potentiometry the critical aspect is what are the different kind of electrodes what you are using. So, by this time you must have realized, one of the major important thing for any kind of measurements of these kind of electro analytical samples, or electro active sample is a reference electrode.

So, we talked about the reference electrode, then you have indicator electrode on which is being used to measure something. So, in terms of the reference electrode we talk about hydrogen electrode, you know what is the challenge of an hydrogen electrode, as a reference electrode which you keep at 0 you cannot have such a so, think of a practical situation, you cannot carry a hydrogen cylinder with you all the time to have your reference. So, you need a simple electrode which could be used as a reference electrode.

So, what people have done over the years, there are two different kind of reference electrode which have been derived with respect to the hydrogen electrode. So, what you can do you could have a hydrogen so, logically think of it. So, I say hydrogen as 0 fine hydrogen electrode, as 0 we have already talked a lot about it. Now I take another half-cell, where I have Ag AgCl and based on that I measure the potential.

So, now I say based on this potential with respect to hydrogen electrode Ag Ag cell electrode is x potential. Now I use Ag AgCl as my reference with that value of this condition. Now with respect to that I can always calculate. So, that is how is the concept of reference electrode became using Ag AgCl as a reference electrode, there is another kind of reference electrode which is being used which is called calomel electrode, we will talk about it.

So, these are the two reference electrode we will talk about, then we will talk about the indicator electrode at two different platforms, one metal electrode the other one is ion selective electrodes. So, give you brief idea.

When we talk about the metal electrode, we talk about the redox reaction happening on the surface of the metal. So, for any kind of potentiometry, you needed to see a change in potential at the electrode surface, it can happen by some oxidation or reduction reaction some redox chemistry or it could happen in the case of ion selective electrode by binding to certain ions across a membrane, or something like what you have seen in a biological cell. You have seen in the biological cell out here if you look at it.

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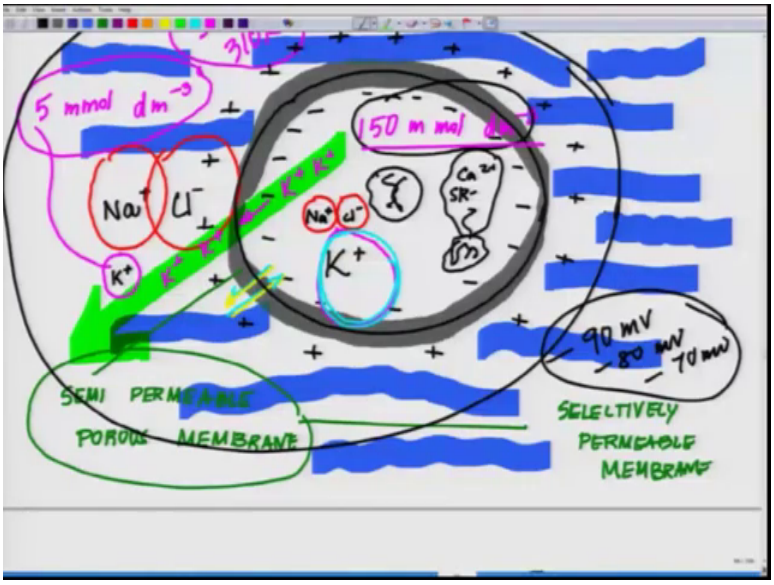

So across the membrane, if you have a specific binding of a molecule something will come to that. So, these are the kind of things what we are going to discuss today.

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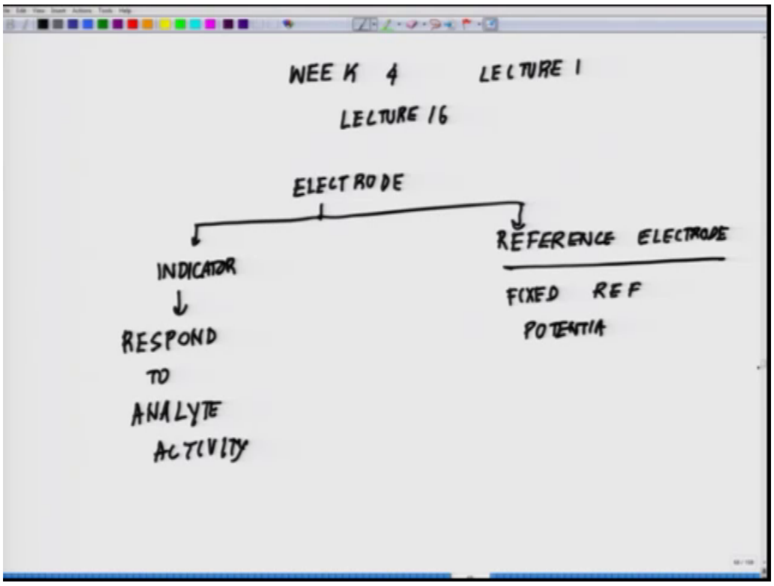

WEEK 4 LECTURE 1

LECTURE 16

ELECTRODE

INDICATOR
↓
RESPOND
TO
ANALYTE
ACTIVITY

REFERENCE ELECTRODE

FIXED REF
POTENTIA

So, to start off with so, we are into week 4, lecture 1, and summary this is lecture 16. So, indicator electrode. So, we talked about the electrode types. So, you have indicator electrode, which is one which respond to analyte activity, then you have a reference electrode which is your fixed reference potential, with respect to this you are measurement doing all. The measurements and the use of electrode to measure the voltage that provide chemical information.

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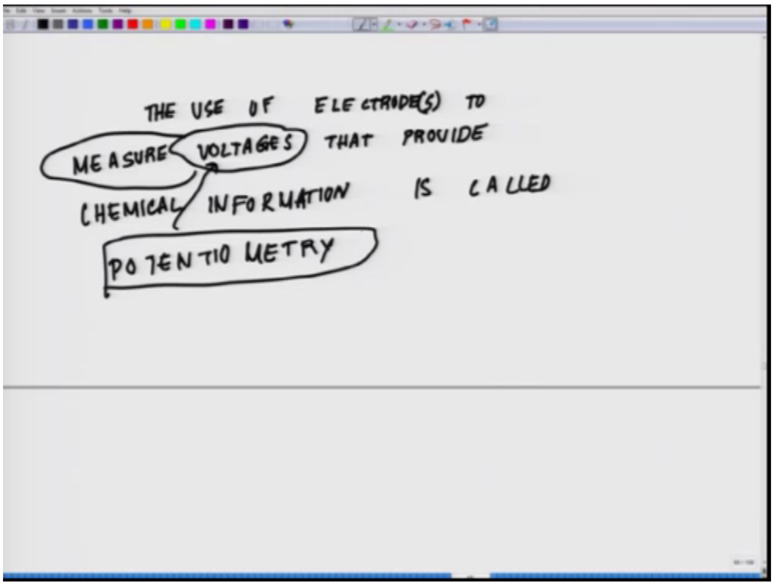

THE USE OF ELECTRODE(S) TO MEASURE VOLTAGES THAT PROVIDE CHEMICAL INFORMATION IS CALLED POTENTIOMETRY

The use of electrode, or use of electrodes to measure voltage, or measures voltages that provide chemical information is called poten tio metry.

So, anything pertaining to potential or anything pertaining to measurements of voltage is called potentiometry. In the simplest case analyte is an electro active species that is part of the galvanic cell, an electro active species is one that can donate or accept electron.

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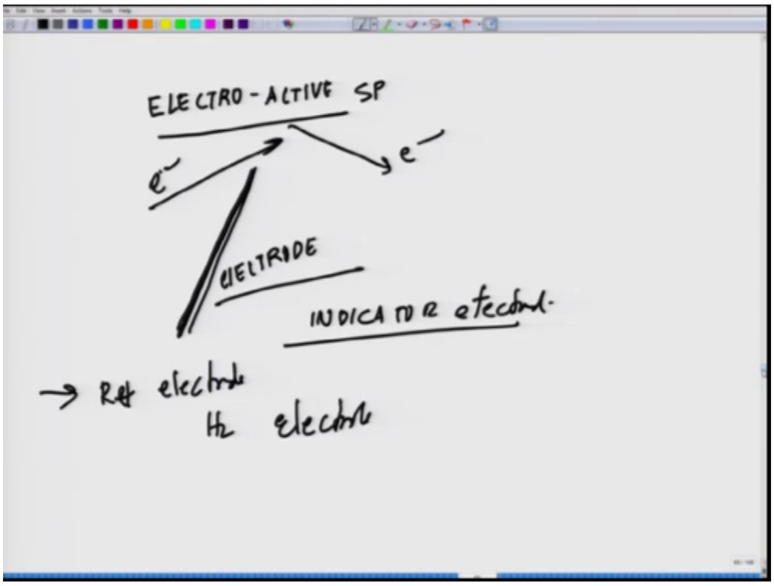

So, electro in the simplest case an analyte is an electro active species, which essentially either there can accept electron, or donate an electron, it could be either beggar for electron, or a donator of electron. And electron which respond to analyte is called indicator electrode.

Now, reference electrode as we talked about, we have talked about hydrogen reference electrode, and I told you that the problem or the challenge of hydrogen reference electrode. And now we will talk about the next silver silver chloride reference electrode, which is also in short called Ag AgCl reference electrode.

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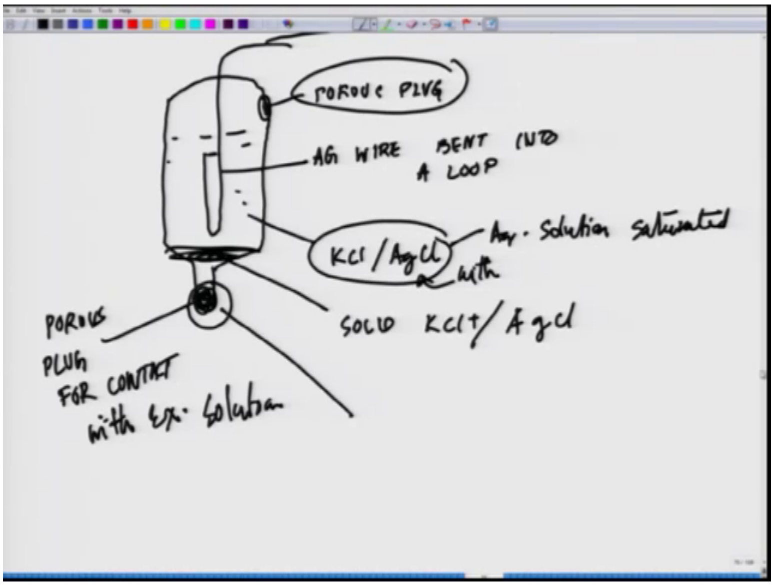

So, Ag; AgCl reference electrode silver silver chloride electrode, is basically it is a half cell. So, this electrode is reconstructed as a thin tube that can be dipped into analyte solution. So, essentially the way it looks like is something like this.

You have other I am just showing you the cross section of it. So, this is how it looks like there is a out here, there is a porous plug Ag AgCl electrode, and Ag wire bent into a loop Ag where bent into a loop aqua solution of saturated with Kcl and AgCl.

So, this is your aqua solution saturated with Kcl, and AgCl and underneath what you observe here is solid Kcl plus some AgCl solid Kcl, and some AgCl, and out here there is a porous plug for contact with external solution.

Here inlet to allow the electrolyte to drain slowly through the porous plug. So, this is the porous plug which is kind of a wire inlet, air inlet, and this is the wire lid, this is how a Ag AgCl electron electrode looks like, and silver silver chloride, and calomel reference electrode are used because they are convenient ok.

The standard hydrogen electrode is difficult to use because, it requires hydrogen gas, and freshly prepared catalytic platinum surface that is easily poison in many solution.

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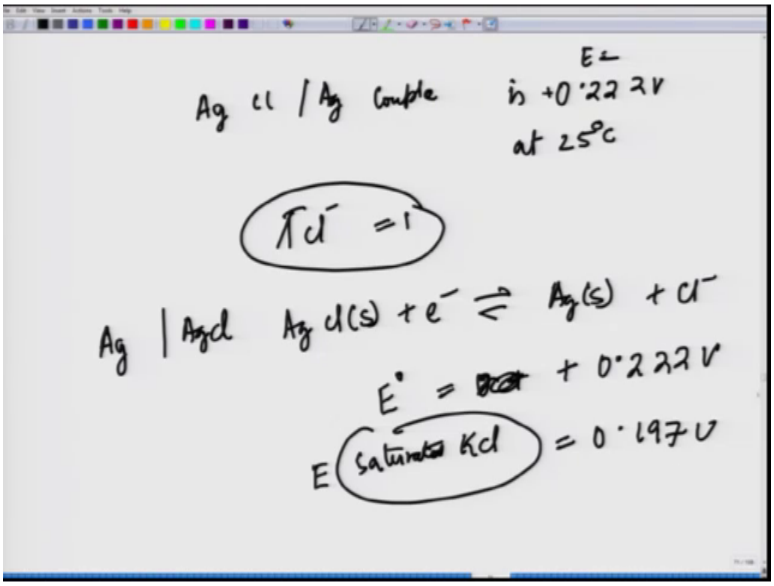

Ag Cl / Ag Couple E° is $+0.222\,V$ at $25^{\circ}C$

$a_{Cl^-} = 1$

Ag | AgCl $AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$

$E^{\circ} = + 0.222\,V$

E (Saturated KCl) $= 0.197\,V$

So, now after showing you this picture, I wanted to go to the standard reduction potential of Ag Cl Ag couple, you look at it is around 0 plus 0.222 volt at 25 degree centigrade, this would be a potential of silver silver chloride electrode.

If this is the potential of silver silver chloride electrode if provided, activity of chloride is unity this part is very important, but the activity of chloride in a saturated solution of Kcl at 25 degree centigrade is not unity, and the potential of a electrode is 0.197 volt with respect to the SHE or standard hydrogen electrode at 25 degree centigrade ok.

So, now when I write this, it you have to write it like this, Ag AgCl where Ag Cl plus electron makes it a g solid plus Cl minus, were E 0 is equal to sorry 0.222 volt, but in a saturated Kcl this is 0.197 volt. The problem with reference electrode is that the porous plug becomes clogged.

So, the porous plug this, these are some of the practical problem you will come across, this plug is getting clogged, there are clogging problem thus causing sluggish unstable electrical response. Some designs incorporate free flowing capillaries in place of porous plug, other design allow you to force fresh solution from electrode through the electrode analyte junction prior to the measurements.

So, mostly these double junction reference electrode, where the inlet inner electrode and outer electrode you have, solution of the outer compartment is compatible with analyte solution say for example, if you do not want chlorite to contact the analyte the outer electrode can be filled with k n o 3 solution, the inner and outer solution slowly mix. So, the outer compartment must be refilled periodically with a k n o 3 solution.

So, these are some of the very first reference electrodes, which get away from the hydrogen electrode or standard hydrogen electrode. So, the idea is that if you use this value with respect to S H E, then this becomes your reference point.

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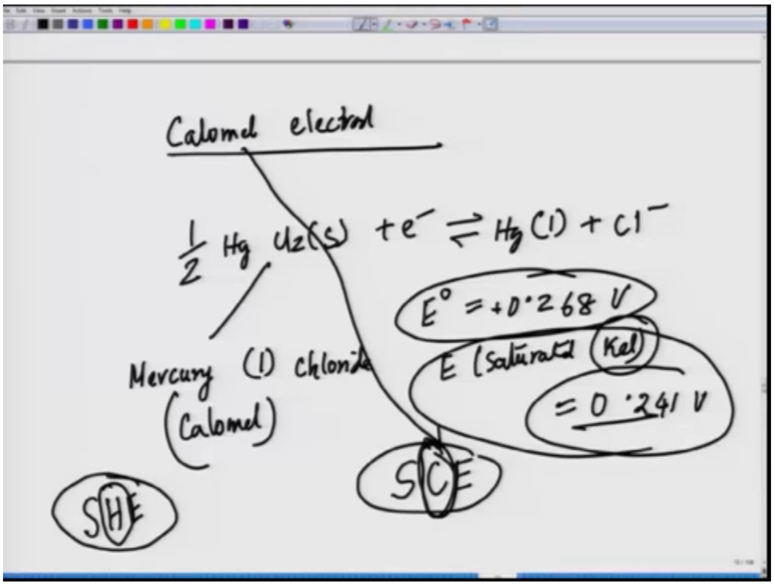

Similarly the next reference electrode is calomel electrode. So, calomel electrode is a mercury based electrode, where I am just putting the calomel electrode reaction first for you AgCl to solid plus electron making Hg liquid plus chloride minus where E 0 of this reaction is 0.268 volt, and this is basically the calomel mercury 1 chloride which is calomel.

But if this is in saturated Kcl the value becomes 0.241 volt. The standard potential for this reaction is as shown here, 0.268 volt, if the cell is saturated with Kcl at 25 degree centigrade the potential is shown out here.

Abbreviated as S electrode with Kcl and is called saturated calomel electrode SCE unlike, SHE which is a standard hydrogen electrode here standard calomel electrode. So, the C stands for calomel the advantage of using saturated Kcl is that chloride ion does not change if some liquid evaporates.

So, you might be wondering why every time you are seeing, the chloride ion is kind of you know out there, why everything is done with Kcl it is a practical significance of it is that Kcl is that chloride ion does not change, if some liquid evaporates remember this. And what you can do? The you can always do voltage conversion between different reference electrodes.

Example if electrode has a potential of say minus 0.461 volt with respect to the calomel electrode, what is the potential with respect to silver silver chloride electrode. What would be the potential with respect to standard hydrogen electrode? You can always calculate it. And I wish you so, you remember this question and try to solve it by yourself, if the electrode has a potential of minus 0.461 volt with respect to calomel electrode.

What is the potential with respect to silver silver chloride electrode? This is the question, and what will be the potential with respect to the standard hydrogen electrode. And in the notes you will have a answer to this question, just you can cross check on the notes, but I will just leave it for you to you know work out. So, these are the two major electrode what I wanted to talk about the standard electrode. Now from here we will move on to the indicator electrode the one which is sensing the analyte.

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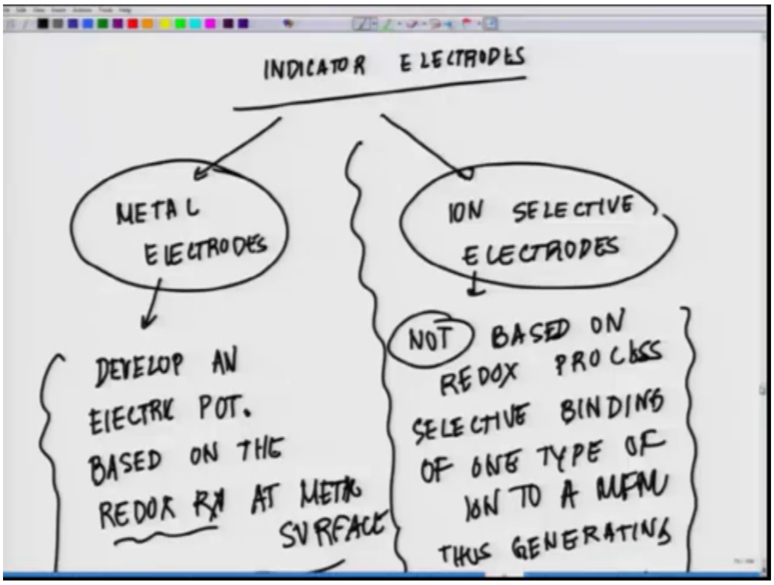

INDICATOR ELECTRODES

METAL ELECTRODES

DEVELOP AN ELECTRIC POT. BASED ON THE REDOX RX AT METAL SURFACE

ION SELECTIVE ELECTRODES

NOT BASED ON REDOX PROCESS SELECTIVE BINDING OF ONE TYPE OF ION TO A MEM THUS GENERATING

So, let us move on to the indicator electrodes indicator electrodes. Now the indicator electrodes you will study the 2 broad classes of indicator electrodes, one will be the metal electrodes, and the other one will be the ion selective electrodes ok.

Metal electrodes and the ion selective electrodes. So, ion selective when we talk about the metal electrodes, metal electrode are the one which develop an electric potential in response to the redox reaction at the metal surface, develop an electric potential based on the redox reaction at metal surface. This is about the metal electrode.

On the contrary when we talk about ion selective electrode, they are not based on, not mind it not based on redox reaction a redox process rather instead selective, instead selective binding of one type of ion to a membrane. Thus generating an electric potential. So, one which is metal electrode which are completely dependent on your electrode based on the redox reaction at the metal surface.

The other one is more like selective binding of certain cations or anions on a particular membrane surface. So, they are very different and interestingly these ion selective electrodes are very popular in biology. So, I will give you an example of where a valinomycin, which is kind of a cyclic peptide which allows the transport a potassium ion inside the biological cell, how the valinomycin could be used.

So, we will talk a little bit more about these different kind of electrodes. So, we have talked about the reference electrode, and now we will talk about the indicator electrodes. And among the indicator electrodes will talk about the metal electrodes, and the ion selective electrodes. I will close in here in the next class, we will talk little bit about these two different kind of electrodes, and then we will move about from there we will move to much of the current measurements, as of now we are only talking about the measurement of the voltage or the potential potentiometry from here, we will move on to amperometry.

Thank you.