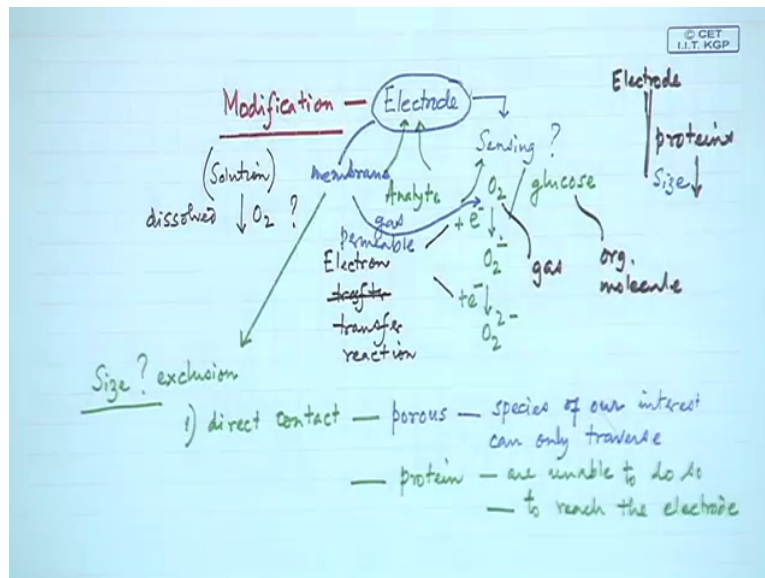


**Course on Analytical Chemistry**  
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**Indian Institute of Technology Kharagpur**  
**Module 12**  
**Lecture No 56**  
**Applications**

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Hello good morning everybody so we are talking about something where we can consider the modification of some electrodes. Why we require that? That is also important and why we are talking all these things is basically important in that respect that whether that developed electrode can be useful for sensing something that means for sensing purpose whether we can use those electrodes such that as we have seen that something is reaching to the electrode in terms of the corresponding analyte, okay.

So when analyte is reaching to the electrode and depending upon its nature whether it is a cathode or anode, we see the oxidation and the reduction of the corresponding analyte species and we can get the corresponding potential for that particular purpose and the number of electrons or the coulomb charge which is passing through that particular electrode. Now if the analyte is electroactive, such that we can sense that particular analyte also it can be your O<sub>2</sub> or it can be simply for glucose molecule that means you have to go for it means we can dump electrons on it, okay.

Such that we can have O<sub>2</sub> minus we call it as superoxide radicals so one more electron if it gets we get O<sub>2</sub>, 2 minus this we all know that how to convert O<sub>2</sub> to superoxide

to peroxide, so this sensing as is very important in this way that how we can sense what you have to strengths? Because O<sub>2</sub> is reaching O<sub>2</sub> is doing something whether a water solution or aqua solution or some industrial effluent has some dissolved oxygen.

So how we can measure the corresponding of dissolved oxygen in terms of the electrochemical methods of analysis or the application of the whatever we are studying in this whole course, so this particular one that means the O<sub>2</sub> if we are able to detect this one or if we are able to detect this or even though you can detect the electron transfer reactions. So this we should detect as the corresponding in terms of the electron transfer reaction if it happens.

If the electron transfer reaction is taking place on the electrode of his we get that particular reaction, so what we see that we are talking something that we are talking something in related to a gas species a gaseous species that means O<sub>2</sub> is going to the electrode and we are thinking that O<sub>2</sub> will get the electron from the electrode, so you have the cathode and cathode is reacting with O<sub>2</sub> and you sense that particular one so this O<sub>2</sub> is a gas molecules then the glucose is a organic molecule and then we can have proteins et cetera.

So proteins can also accept alternate electron in terms of the corresponding attached electrode so if it is close by some electrodes, this is electrode, so this more and more complex species starting from the gaseous species to that of your proteins species if it is nearby to that of the electrodes, it is not that all electrodes can sense the presence of this in terms of the electron transfer activity.

So we can go for something that is why we require the corresponding modification of those electrodes and the modification in terms of these basically give rise to something that this size of this that means the protein sizes pretty big and gas we know that something is that we can have some screen or the membrane which can permeate the gas molecules, so because there are different sizes of these gases also like O<sub>2</sub> and 2 and all the properties also different.

So this thing that means the modification in terms of the electrodes so we can cover the electron with some membrane and if the membrane is gas permeable, so if this membrane what is enclosing your electrode is gas permeable and only allows the O<sub>2</sub> to reach the electrodes, so we get something that we can have corresponding size is very important and as a result we get some membrane so you have the membrane you bring the membrane and related to size also.

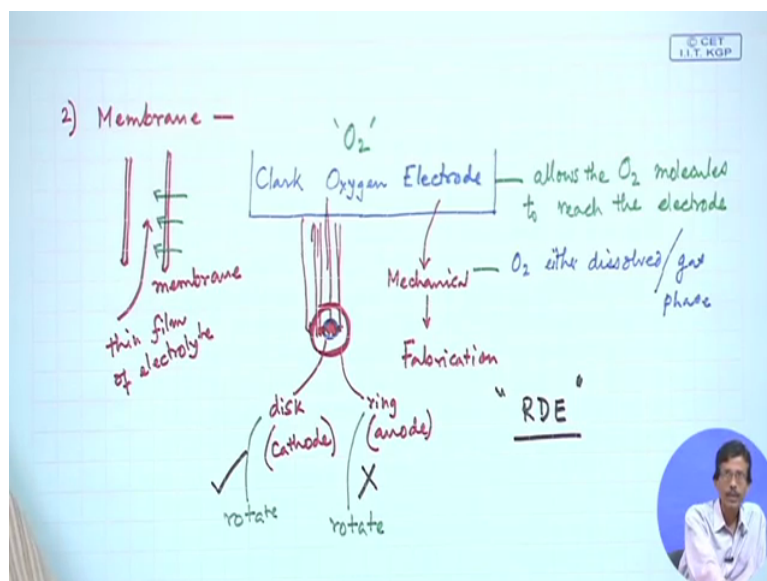
So that is sized exclusion that means basically what we do in terms of the filtration with the paper, filter paper or a corresponding membrane type of thing that is the cloth, the polypropylene cloth we always know that, that also filter it out, so there is some sort of filtration we can have and the size exclusion membrane should be there, so this size exclusion membrane will be there and we will not allow that is the direct contact, what we are looking for direct contact of the electrodes.

So we know that when we have the normal hydrogen electrodes and hydrogen gas is bubbled nearby the electrode at a particular pressure and we know that a special type of electrode is required to detect that particular presence of hydrogen and its electron transfer in terms of its electrode property as normal hydrogen electrodes. So this direct contact with the electrodes, what we do? We can go for something that is the size exclusion membrane we can put, so we should go for something which is porous.

So a porous again the porous membrane we should fix and the species of our interest that means whether it is a proteins or a O<sub>2</sub> molecule that means the gas molecule, so the species of interest can only traverse, so species of interest can only traverse such that it can reach the corresponding electrode. So when this is there that means if something is there that means if we think that is only permeable to gas particularly the O<sub>2</sub> molecule, the O<sub>2</sub> gas molecules so if we have some mechanism where the porous membrane is attached and that porous membrane and only allow your O<sub>2</sub> molecule to reach the electrode but will not allow the bigger molecule having some kilodalton molecular weight.

So it is basically a big organic mass polypeptide several polypeptide chains are there and that mass is also there it can be 50 kilodalton or 80 kilodalton or 150 kilodalton of the mass, so this protein will not go so protein is unable to do so, so if you allow to think of the direct contact, so proteins the protein mass is basically, the protein are unable to do so that means to reach the electrodes, so the protein molecules will not reach the electrode so we must have some different mechanism. If you try to use the corresponding electron transfer action or electron transfer behaviour for its potential as well as the rate of electron transfer for the protein molecule we should have something different in mechanism.

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So this is one that means the porous art is there so now we can have that membrane if you put the second mechanism is the membrane which is very important for your O<sub>2</sub> determination. So we put some membrane, so membrane can separate those species so is a thin film of electrolyte can also be a membrane, so if we have the membrane so if we have the electrodes and we say that we can have some porous membrane but in between in between we can have a thin film of electrolyte.

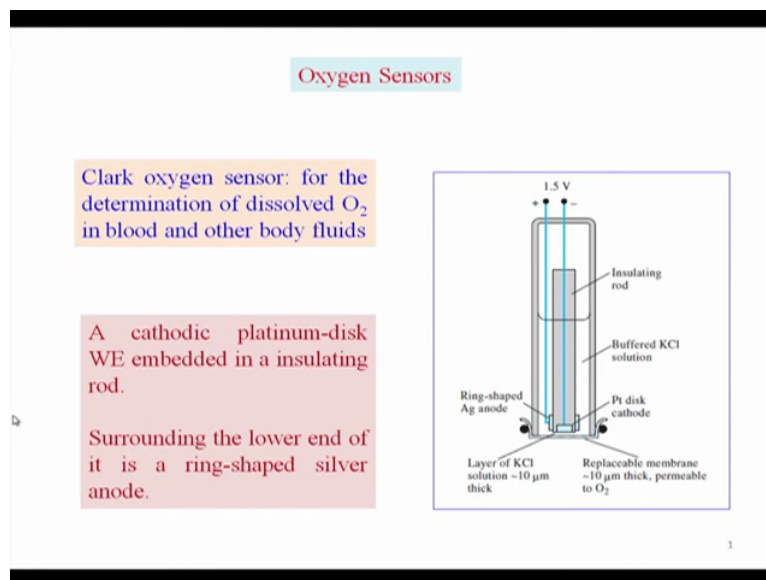
It has certain advantages, so this particular one if membrane can allow some species to go inside then thin film of electrolyte is another check, so one particular such mechanism that we will study now or that we will see how it is develop or how it is framed is a we call it as a oxygen electrode that means it can sense the oxygen that means like your hydrogen electrodes it is very easy to remember that we that is a normal hydrogen electrode, so we have the oxygen electrodes and the person who introduced this having a surname is Clark so the scientist Clark invented that one so is a Clark oxygen electrode.

So what it does is does basically that means it first thing that what modification we make on the electrode and the electrode surface such that some material like that of your O<sub>2</sub>, O<sub>2</sub> is our interest, so this O<sub>2</sub> molecule can reach so how you get that particular electron because we are talking in terms of this electrode. So it allows the O<sub>2</sub> to go allows the O<sub>2</sub> molecules rather to reach the electrodes. O<sub>2</sub> molecules to traverse O<sub>2</sub> molecules to pass means it can reach the electrode by passing through this membrane.

Okay so this particular one so reach the electrode to traverse the membrane so it is passing through the membrane then what happens that O<sub>2</sub> can be dissolved in the thin film of this particular electrolyte, so if we have the thin film is a very small film on this we know that when we dip a solid electrode or a solid surface on some any liquid, so liquid can form a film on that particular solids surface or the solids support, so electrode is your solid support and on that electron if you have that film and that film can dissolved this O<sub>2</sub>.

So O<sub>2</sub> either dissolved or present in the gas phase, that if it is not dissolving in the thin film of electrolyte it is present in the cavity and it is basically trapped. So that is the corresponding mechanism that how we develop and how we grow that particular electrode which is your oxygen sensor so we get the different types of this oxygen sensors over there and how we can develop those oxygen sensors but the very first thing of that developing oxygen sensor is your developing the electrode, otherwise the mechanism for making your measurements for all these things whatever you measure, the measure the current because definitely the sensing mechanism is the corresponding amount of current what you can detect in terms of the corresponding oxygen presence in it.

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So it is required for why do we require that oxygen sensor? So is basically the development of the electrode and that electrode we can consider as a sense, it can determine quantitatively and do a very low concentration level, the dissolved oxygen in any solution we are talking about that industrial effluent, the environmental material, the water from the sea, water from the river, water from the lake anywhere.

Because as we determine in terms of the corresponding talking in terms of the water pollution is a real headache for the chemist, is a headache for the environmentalist and headache for the other people also. So we know to terms basically we can the chemical oxygen demand and the biological oxygen demand the COD and BOD values for this water molecules because in that particular case if we talk in terms of the corresponding demand of oxygen, the one is the chemical oxygen and another is the biological oxygen demand store

So what we can think of that how much oxygen it can take by the species present in it whether it is a chemical waste or a biological waste for any industry or any other activity, human activity can give rise to that particular demand but now the amount of O<sub>2</sub> even the pure sample of water we do not know how much your sample of water if you have and what amount of water you should have.

So if you have a very handy electrode type of thing or a sensing type of thing can determine the amount of oxygen and what you require for the water what you are putting for your aquarium also because aquarium has some amount of dissolved oxygen otherwise the species which is living over there the aqua species that means fishes and other things will not survive.

So this is one aspect and another is also is how much is there in our blood and any other body fluids because the dissolved oxygen in the blood is also important it is not that whatever amount of oxygen you have which can be transported to the cells by your mechanism through haemoglobin and myoglobin. So these are the oxygen binding molecules or oxygen binding metal or proteins because you have the metal ion iron is there so this oxygen binding metal or proteins which are involved over there.

It should get a particular amount of concentration of O<sub>2</sub> because you look for some oxygen saturation with respect to the myoglobin and haemoglobin and these 2 very important and interesting molecules are there one is required for storing of oxygen and another is require for carrying the oxygen or transportation of oxygen for the regular use that means what we use that we require those oxygen for burning the food material.

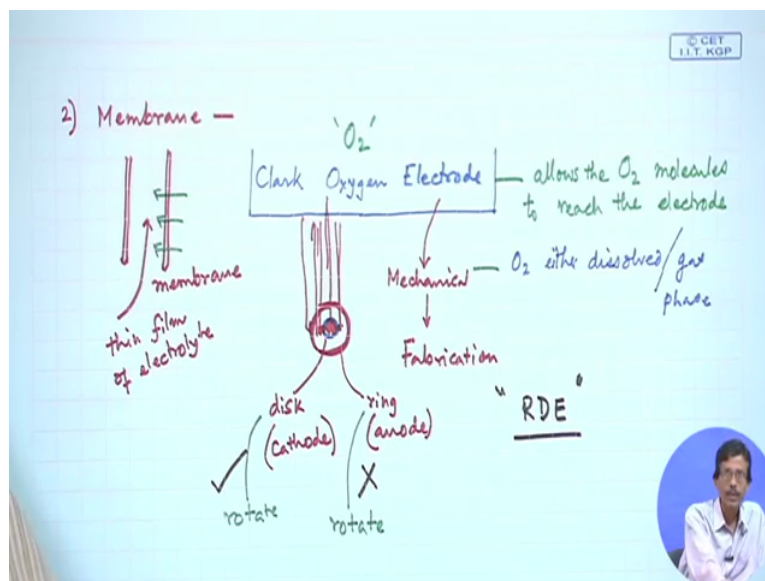
So the basic formulation or the basic framing of this is very simple is one example from again Skoog books in any other book also you can have the corresponding simple line drawing for this but he basic thing what we are looking for you have 2 end of the electrodes and you see that the power requirement for this is also your dry one single dry cell battery power is 1.5 V, so this 2 ends the positive end and the negative end so what you have, so the negative end

means the corresponding one which we use as the corresponding cathode is ending at a Platinum disc electrodes.

So you have a Platinum disc cathode, so you can have that for hydrogen electrode also use Platinum the most possible inert metal ion which will not react the species either from the solution or the industrial effluent or the gases itself. So basically this is the bed I mean it is basically a disc very small circular shape disc is there and this is connected with this electrical connector to the negative end of the battery or the power source and you have something that you have some insulating rod such that it is separated from your other material which is your anode material.

So you have the in selected rod can be a graphite rod, can be any other carbon rod, can be other ebonite rod or anything, so you have the insulating rod so insulating rod and the cathode is making and you have the other one that means the ring shape anode that means you have the thing that will discuss very quickly that you have.

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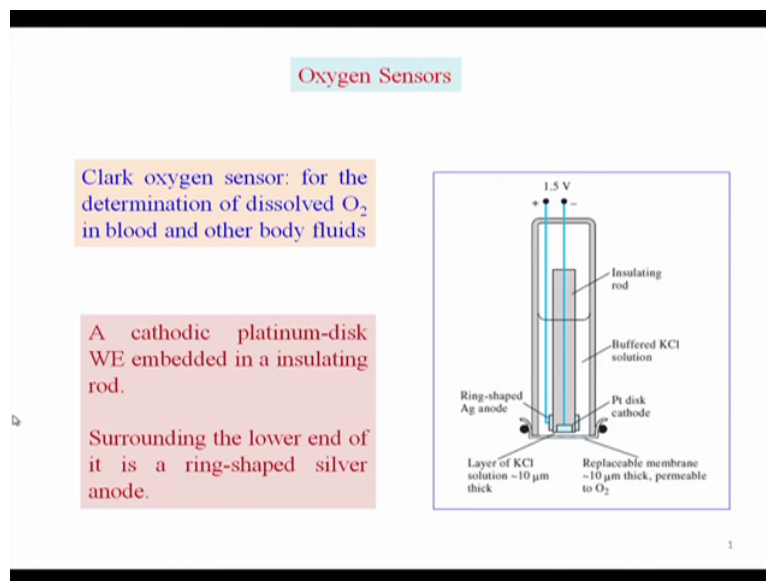


This one is the disk so you what you should know because this has also the development of a the type of the electrodes, so the mechanical framing, the mechanical framing of the electrode is very important. So this the mechanical engineering can do so the mechanical thing is required for your fabrication, how you who fabricate the electrode, so this is your disk part and outside you have the corresponding ring, so this mechanism we should know that the inner one is your disk and the outer one is your ring, so if this is your cathode, this is your

anode and you get you get everything at means everything is enclosed in the corresponding inert material and you have the connection.

So outside you have one connection and inside also you have the other connection because it is covering so once it is connected it can get that thing and inside you have other connectivity, so this is the thing that if you are asked to draw it also you will be able to draw and you should also be able to tell others that how this framed.

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So you have this that means the Platinum cathode so it is there as a disc and surrounding this is your ring-shaped anode but this is made of silver because you have the corresponding potential differences and all these things, so this is therefore the electrode the material what you are using you should always be very much careful to know that particular material what you have at electrode materials so at one point because it is a very small amount only very little amount of Platinum and little amount of silver require so that is why it is not so costly.

If you compare a corresponding labour charge for making or fabricating the particular electron, so materials wise it is not much costly but the fabrication wise it should be costly enough, so you have the silver electrodes and what you put, you put a buffered KCl medium that means what we know that when we write any cell or half-cell we know that the KCl is there and silver is present.

So this thing is also there so buffered KCl solution is there and now what we are talking just now that you can have a corresponding thing that means 2 things are there, the first one is your membrane which is outside your electrode, so membrane so it can be replaceable also



because after some use after several experiment you replace that, it is of only 10 micro-meter thick and which can permeate your O<sub>2</sub>, so if the thickness of that membrane whether it is a polypropylene cloth.

We consider this as a polythene cloth the polypropylene the PP cloth or any other materials of that thickness but it should allow oxygen to pass and you have another very thin layer of KCl solution so it is buffered in KCl and if the layer is there that means what we have just now have seen that you have a corresponding separation that means a thin layer of some solution, thin layer of liquid and that is of that particular entities of the same thickness in the range of 10 micro-meter thickness.

So what you get, you get a porous membrane and covering that particular one is a corresponding liquid membrane, so this is a very simple fabrication for that electrodes is simply that you dip the thing and you measure the corresponding kind due to the reaction of this O<sub>2</sub> reaching the cathode. So a cathode Platinum disc you have which is your WE is your working electrode and an embedded in an insulating rod just now what we discussed so you can have that thing in writing.

So that you should keep in your mind and which surrounds basically a lower end is a ring-shaped silver anode, so is a ring, so you have the disk and you have the ring, so is a silver, so you get this particular thing that a particular arrangement which is known as your ring disk or disk spring electrodes.

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The tubular insulator and electrodes are kept inside a second cylinder that containing buffered solution of KCl

Thin (~20 μm) oxygen permeable membrane of Teflon is held in place at the bottom end of the tube by an O-ring. Thickness of the electrolyte solution between the cathode and the membrane is 10 mm.

O<sub>2</sub> diffuses through the membrane into the thin layer of electrolyte immediately adjacent to the disk cathode, then diffuses to the electrode for reduction to water.

Two diffusion processes are involved: one through the membrane and the other through the solution between the membrane and the electrode surface.

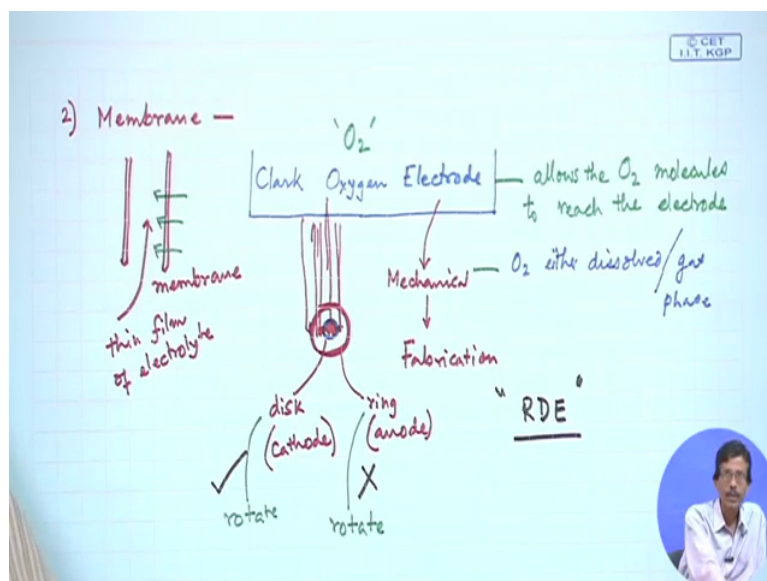
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So the insulators through which it goes get inside the second cylinder and containing buffered solution of KCl, so the tubular insulators and electrodes, so a insulators is there and electrodes are there which is kept again inside a KCl solution and sometimes tented 20 micro-meter of permeable membrane now you see like polypropylene you can also use a Teflon, so Teflon we all know is a home-made now there is a use in the home maximum so the Teflon coating on the kitchen wires and all these in kitchen you get the Teflon so is a very useful material.

So is basically a membrane of Teflon is placed at the bottom of the tube by O-ring and thickness of the electrolyte solution between the cathode and the membrane is again only 10 millimetre. So this 10 millimetre to 10 micro-meter of this we can handle for reaching that particular oxygen for a typical diffusion, so adjusting to the disk cathode and then refuses to the electrodes for reduction to water, so what we are looking for we are looking for the reduction of O<sub>2</sub> to water.

So that is the only reaction what we are looking for as I told you so we are not going to those services that means we are looking for action of O<sub>2</sub> to superoxide to peroxide so we are not going for that, so anything and also happen over there that means the fate of the oxygen in one way it can go to superoxide to peroxide and in other way it can go to formation of water molecule having a different electrodes potential for the formation of water molecules from your O<sub>2</sub> molecule. So to diffusion processes are therefore are involved, they are taken part actively for this measurement process on through the membrane and other to the solution between the membrane and the electrodes surface.

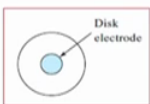
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So first it goes through the membrane as I told you that it is passing through the membrane, so it is crossing your membrane so this membrane it is crossing. So it is also a diffusion process and between the membrane and electrodes surface you have a thin layer of that electrolyte it should also pass through that, so if the traverse of those molecules that oxygen molecules is deficient controlled, so it should have 2 barrier one is the typical membrane and another is your thin film of electrolyte.

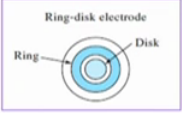
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Hydrodynamic flow of stirred solution is based on measurements made with a rotating disk electrode (RDE)



The rotating ring-disk electrode is a modified rotating disk electrode that is useful for studying electrode reactions

When an electroactive species is generated **at the disk**, it is swept past the ring where it undergoes a second electrochemical reaction.



Such studies provide much useful information about mechanisms and intermediates in electrochemical reactions

So you get 2 different division processes so this particular thing that means the flow of those gaseous molecules we can consider it as the hydrodynamic flow of stirred solution if we have, so if stirred the thing so what we basically get that thing so is in an aqueous medium and

you just stir the solution since dynamics is there so hydrodynamic flow of stirred solution is based on measurements made with a rotating disk electrode if we can have, so the mechanism is also so what you know that now we are bringing something which is the little bit complex not very much complex because you have the disk, you have the ring.

Now you do something again something what we have the stirring thing that means we rotate we can rotate now, so is the rotating of a particular range so even rotate the ring nicely, so you have the corresponding rotating disk electrodes, so with a rotating disk electrode so the ring can be rotated and the disk also can be rotated. So what you rotate so this is a very complex process related to your diffusion and the hydrodynamic flow of the analyte, so you can have the option that you can rotate the disk as well as can rotate the ring.

So one electrode what we will find and we can only learn also that if we abbreviate it as RDE, the rotating disk is there so you are not a rotating the ring so rotating disk electrodes so this is one type of electrode that we can have of the same formulation or same mechanism what we get, so you get that so you have just now what I have drawn you can also get this from any book and you can also draw yourself that what does it mean what is the thing that if you giving the diagram also a level it.

So it is in terms of this particular classes that means the electrochemical classes where we try to understand everything in terms of the corresponding thing and this is basically a very simple type of electrode that what are the shapes of those electrodes we should always know that when you have hanging drop of mercury.

So drop of mercury so hanging drop of mercury and give rise to electrode and what is a shape, the shape is known that is have the thing that through which a capillary is there so it is a very (27:18) capillary is there and you get a corresponding drop forming because depending upon the size of this capillary this corresponding internal diameter, you get that corresponding size of this mercury drop.

So we get dropping mercury electrode and this dropping mercury electrode is that through capillary where going for this drop and for some time that it has some lifespan it is hanging, so life when it is hanging from the bottom of this capillary or the corresponding solid surface of that electrode, so this dropping mercury electrodes you can have so you should be able to draw the shape also the ring-shaped or the disk shape thing is also there.

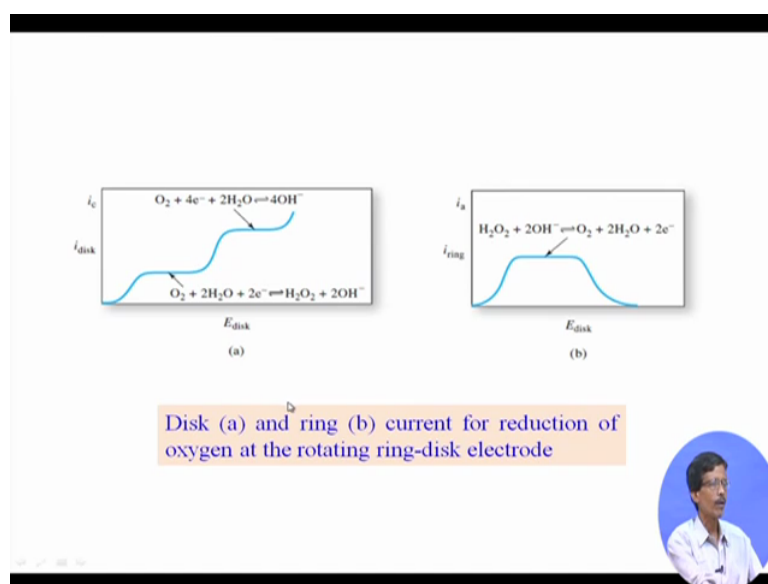
So if you now the rotating ring this electrodes is a modified rotating disk electrodes, so rotating ring disk electrodes, so this is their and ring is there as a we know now, so if you have ring as well as disk now with the rotating disk electrodes it is useful for studying different types of electrodes reactions. So now you have the disk and you have the ring surrounding this particular disk and everything you have this particular one, so you can have the option that you can rotate the disk you can also rotate the ring.

So when an electroactive species is generated at the disk, so disk is basically generating that electroactive species that means what you have that means if the disk is taking that or supplying that electron for your reduction to your  $O_2$  species it is forming your  $O_2$  minus or you can go to  $O_2$  minus that means the oxide ion but in this particular case when it is rotating something that it swept passes the ring where it undergoes a second electrochemical reaction that means it is passing from here and going or reaching to the ring and there it goes and taking some other reaction because it is a electrodes of different polarity.

If the disk is cathode your ring is anode, so after getting that thing is reaching the anode so you get something which is different but what you looking for is basically a cyclic process the way we have understanding the thing in our cycling voltammetric measurement that you do first oxidation then you go for the reduction. Here also the disk is doing something that means if it goes for reduction in terms of a cathode present in the connection for its disk when it reaching the ring then the ring can go for its corresponding oxidation.

So all these studies provide very useful information about mechanisms and the intermediates in the electrochemical reactions, so this will be a much more complicated process you should know little bit only at the modification of those electrodes and provide more and more useful information terms of the corresponding thermodynamically control electron transfer or thermodynamically control the corresponding and kinetic behaviour, so what we find that is that for important that well you go for the corresponding kinetics and all these measurements.

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So if we have these 2 that means if we have the disk as well as the ring in hand, so we can have 2 different currents in our hand, so separately we can measure because we can measure as we know that working electrodes something which is your cathode, working electrodes can be your anode also, so you have a disk A is the disk current and B is the ring current what we get, so for reduction of oxygen at the rotating ring disk electrodes.

So is the rotating ring disk electrodes, so we can also consider the rotating disk electrode or rotating the ring disk electrodes we can consider, so what we do we just basically plot again it is the current potential plot what we studied earlier, that now the potential of the disk is plotted against the current of the disk and in other case the potential of the disk is plotted against the current of the ring that is the only difference.

So these 2 are different the shape of this plots will also be different but the basic reactions for this is all same that is the electron acceptance by the  $\text{O}_2$  molecule for its reduction and your corresponding  $\text{O}_2$  is also reduced for your hydroxide ion formation as well as the water formation. So here also this thing is also the reverse reaction what we get that is your  $\text{H}_2\text{O}_2$  plus  $2\text{OH}^-$  minus what is on the right-hand side what is forming because this has been formed.

That means hydrogen peroxide has been formed by the disk so it will be reaching to the ring, so ring current is due to the again that corresponding reaction of hydrogen peroxide that means the oxidation of the hydrogen peroxide, so you see that this particular reaction that means this current is you have a plateau and then again it is falling depending upon the concentration of the  $\text{H}_2\text{O}_2$  what is reaching over there, so the corresponding sense of the ring

current is completely different. So these 2 plots basically will be useful when we talk in terms of the corresponding development of the electrodes. Thank you very much.