Industrial Instrumentation
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Lecture – 32
Dissolved Oxygen Sensors - II

Welcome to the lesson 32 of industrial instrumentation, this is a continuations of lesson 31 actually, the we will consider here the dissolved oxygen sensor. We discussed dissolve of basic principle of the dissolve oxygen sensors in details, in the lesson 31. This particular lesson, we will consider the different types of electrodes, it is calibration type of membrane, these are the very important things for designing any D O 2 probe and type. I mean, type of materials which is used for making the for making the electrode specially, the electrolytes and what should be the suitable nature of the membrane also that is also very important.

Because in some cases, you have to sterilize the dissolve oxygen sensors, when it is used in the bioreactor or you will put in the autoclave. So, the minimum temperature, they are be 120 centigrade. So, in that type of situations, we will discuss we need some sort of some sort of autoclaving and with a or some, some sort of sterilizations. And at this particular lessons, we will discuss all those in details it will be a as I told you earlier, that is it is a continuations of the lesson 31, let us look at the contents of this lesson.

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Lesson 32 dissolved oxygen sensor 2 contents. Construction of electrodes, how the electrodes? What is there? What is anode? What is cathode? What type of material used for the making anode and cathode? What type of electrolytes we are using where the membrane lies? So, all this things we will discuss, then Clark-type electrodes, we will basically, consider 4 different electrodes. So, that we will discuss, 1 by 1 what are the advantages? What are the disadvantages? What are the relative I mean, relative properties of this particular electrode, that we will discuss. Then Mancy, Mancy electrodes, this all this name actually, given by some inventors. So, those are most widely for bioreactor, so that we will discuss in this particular lesson. Mackereth electrode, then you have Borkowski and Johnson electrode. So, these are the 4 different electrodes we will discuss in this particular lesson.

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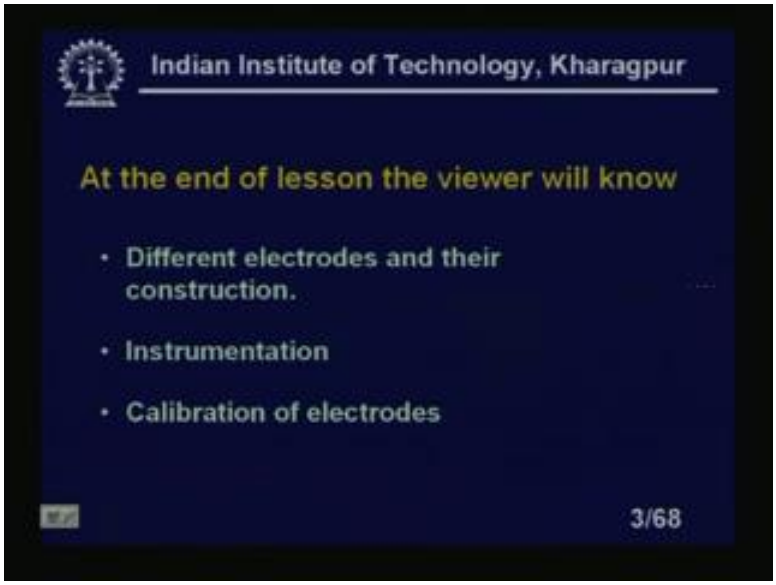

At the end of the lesson, the viewer will know, different electrodes and their construction 4 different electrodes, how they are, what are their construction? Instrumentation necessary, because you see, that it is usually, the current, which you will get from the dissolved oxygen's is very, very low. So, what type of precautions? We will take all those things; we will discuss in this particular what type of amplifier? We will use all these things; will be discussed in this particular lesson, then calibrations of electrode, because calibration is most important. So, there are I mean, we can calibrate, it in 3 different conditions, either in the partial pressure dissolve oxygen concentration, all this things will be discussed in this particular lesson.

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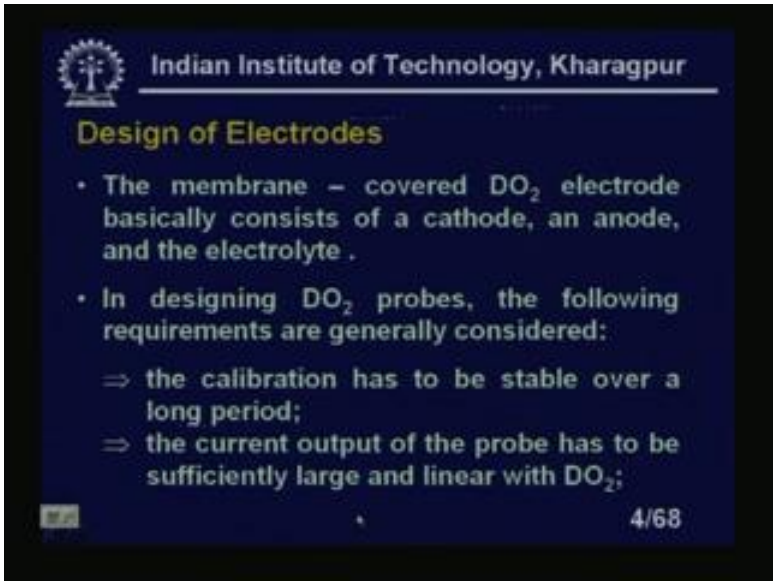

Design of electrodes the membrane covered D O 2 electrodes, basically consist of a cathode an anode and electrolyte it is basically, it is a probe like a p H probe. So, it has same thing, we have a D O 2 elect, we have a cathode, we have a anode. And the electrolyte one thing, we are missing here, we are talking about there is a membrane anyway, it is a part of the. So, electrolyte is most important as I told you, so there is the 3 parts one be cathode, one be anode and one be electrolyte also, there will be membrane. In designing D O 2, D O 2 means, dissolve oxygen concentration. So, dissolve oxygen as you know actually, we are measuring partial measure that is converting into the concentrations.

In designing D O 2 probes the following requirements are generally, considered what are those requirements? The calibration has to be stable over a long period usually; you know that in bio reactions. It takes a long time some of the reaction takes over, several days to complete the reaction no reactions will be less than 72 hours, some even longer. So, the stability of the calibration; that means, whatever the reading it is giving there are many problems, you will find there is a depositions on the cathode those things are there. So, it will change the calibration. So, we have to avoid that type of I mean, change of calibration otherwise entire output will be wrong.

So, this to very careful, so the stable of calibrations is more important. So, calibration has to be stable over a long period number 1. The current output of the probe has to be sufficiently large and linear with D O 2, D O 2 mean, dissolve oxygen concentrations or

partial pressures of the oxygen. Whatever way you say right, it should be linear that is most important otherwise if it is non-linear. So, it is very difficult to calibrate. So, it is linear is that is I mean, basic principle or the basic desirable characteristics of any instrumentation system or instrumentation sensors.

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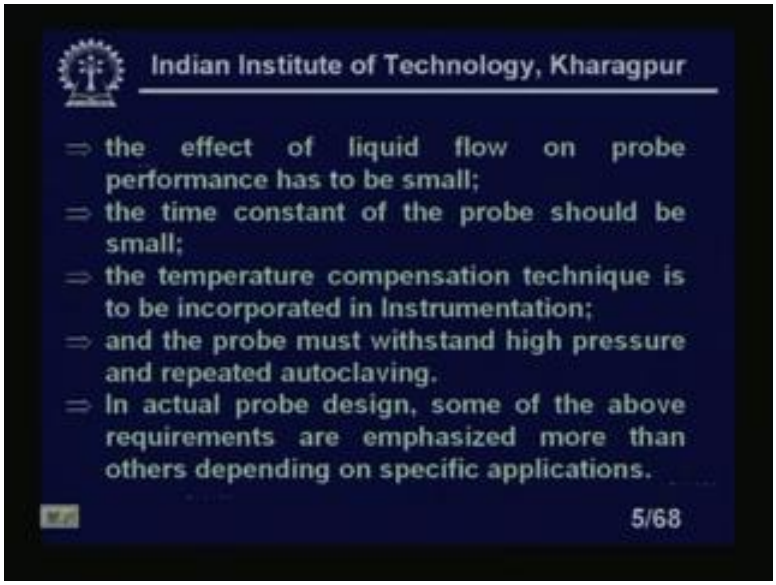

So, we will consider this thing then we have the effect of liquid flow on the probe performance has to be small the, if we suppose we are putting this probe on a liquid which is moving. So, in that types I mean, cases, so the liquid flow on the, because there is a permeable in membrane through which a liquid may come in or the the electrolyte may go out. So, those, things is to be cleared of this needs to be think of. The time constant of the probe should be small, this is another important thing time constants of the probe should be small the temperature; that means, the response time should be very fast. That is I am talking about the response time should be very fast or the time constants of the probe should be that is desirable, because sometimes we will find it is out of our control. So, we will try always, to make the time constants, we will see that some, some conservation. If we particularly, design this electrode in a way, that by which I can get a fast response time.

Usually, you know the bioreactors, we are much not much concerns with this thing you will find that the most of the bio reaction cases. We will find the time constant is typically, large right suppose, I have a I am there is a reactions, which is going on for seventy 2 hours. So, you will find or 48 hours. Even if you sample the each sensors

output 10 minutes 6 minutes 10 minutes that is to be considered to be quite high also. Because any reactions, it takes a long time it does not change that rapidly, that you have to sample every minute. So, the time response, we should not give much emphasis on this, but sometimes we need we have to take some action suppose I mean suddenly. The dissolve oxygen concentration or partial pressure of the oxygen falls. Immediate action is to be taken in type of situation; obviously, if you have a lower time con I mean time constant of the fast response of the sensor that is always helpful for taking actions and all those things anyway.

Temperature compensation technique is to be incorporated in instrumentation, because as you know, that if the temperature changes. So, so many properties of the, of the probe will change. So, that will change, because the electrolyte properties will change. So, there is some sort of temperature compensations or the more precisely, I should that the ambient temperature compensation should be incorporated, that is a part of instrumentations. Then we have the probe must withstand high pressure and repeated autoclaving, this is also problem, because you know that in a in a bioreactors. Whenever you we are using the sensors so; obviously, one important thing, we have to make autoclave. You have to sterilize autoclaving some sort of I should say, it is like a pressure cooker all of you have a household like a household pressure cookers.

Which you have seen usually, the temperature of this pressure cooker I mean, inside temperature. You have to rise it if mean, if you have to raise the temperature suppose 120 degree centigrade something, we have to increase the inside pressure, so so the probe should withstand that high pressures as well it is; obviously, more than atmosphere. And high temperature repeated autoclaving also is I mean, one of the desirable properties having a good, good probe. In actual probe design, some of the above requirements are emphasized more than the others, depending on the specific applications; you cannot get all this things on a single probe design. We have to dispense off some of we have throughout, some of the requirements we have to take, some of the requirements the most which is more important for our particular applications.

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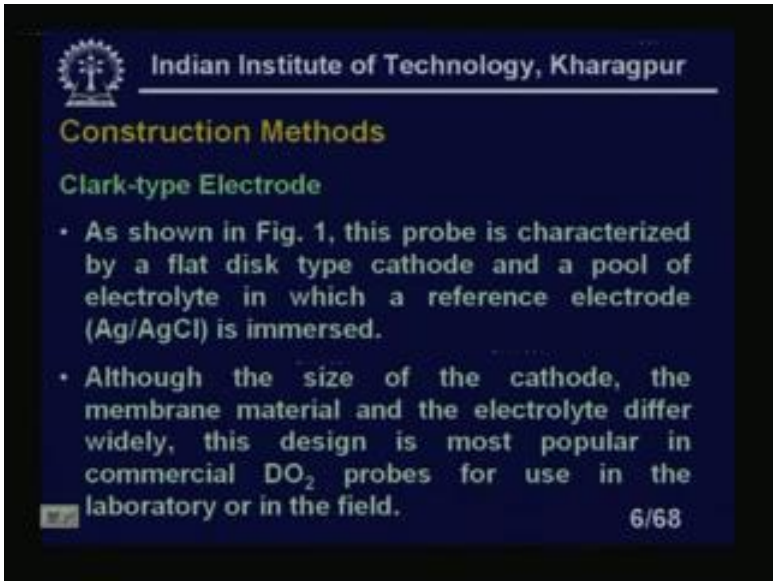

Construction methods Clark type electrode let us, look at as have shown in figure 1, which will come after sometime, that this probe is characterized by a flat disk type cathode. And a pool of electrolyte in which a reference electrode, which is A g by A g and C l silver chloride is vast right. So, that is the basic electrodes, we have seen we will show that in the figure. Although the size of the cathode the membrane material and the electrolyte differ widely, this design is most popular in commercial D O 2 probes. For use in laboratory or in the field, this is the best most common sort I mean, this is a electrodes that is the reason. We have put in the position number 1 the Clark type electrode let us go to the details of this.

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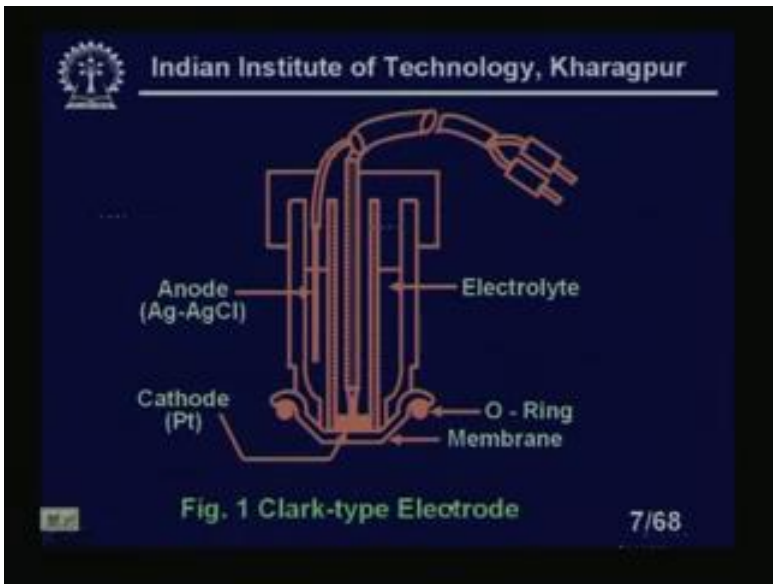

This you see that, the figures this, a Clark type electrode, you can see here, we have a anode A g, A g and C l cathode. We have which is made of platinum, then you have membrane usually, this membrane is made of Teflon, there is a O ring it is like this one which is to be tightly put. So, that the membrane will be in contact membrane will be in will hold in a position. And we have electrolyte throughout the medium, you see the electrolytes are here right. So, this is our, I mean this is the 2 probe output, this is a 2 wires is coming out, which is to be which is to be connected. You can see here 2 wires are coming out. So, through which I will measure, I will show the circuit, how we will measure that current right? So, this is our basic Clark type electrode.

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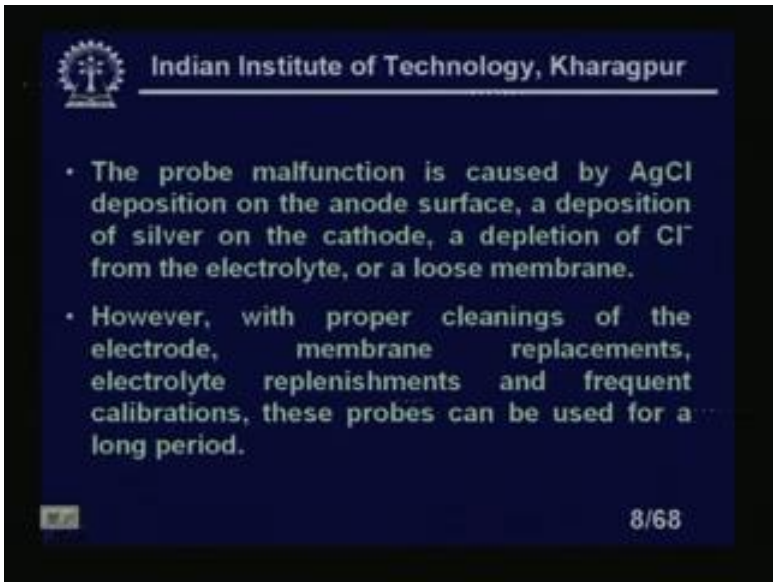

The probe malfunction is caused by A g C l deposition on the anode surface and depositions of silver on the cathode a depositions of the silver on the cathode and depletions of chlorine from the electrolyte or loose membrane. So, loose is to be this membrane is to be very tight. So, that is the reason, we are using a o ring, which is will put the membrane very, because you have seen you see here, there is we have a membrane here . So, you have a membrane here, we have seen, so this is to be tightly so that no electrolyte will come out, you can see here cathode and anode is there. So, caused by A g C l depositions on the anode surface; that means on the platinum surface and depositions of silver on the cathode, which is a platinum and depletion of C l from the electrolyte or a loose membrane, these are the most important.

However, with proper cleanings of the electrodes membrane, replacement time to time replacement of the membrane. And electrolyte the frequent calibrations these probes can be used for a long period. So, this types of probes can be this is a very I mean, very I should say very obvious, sort of I mean, any sensors. We will use, we have to be need frequent calibrations any probe, whether it is a p H or measuring the I mean, conductivity or ((Refer Time: 12:41)) dissolve oxygen concentration. Everything we need some this type depositions will be there, we have seen the polarizations all those things are there. So, it is to be, so repeated cleaning then of the electrolytes or it is supplied from some reservoir permanent reservoir. So, that type thing; obviously, will make the, and frequent calibrations will make I mean, make the same for a longer use, longer use over the over the period of time.

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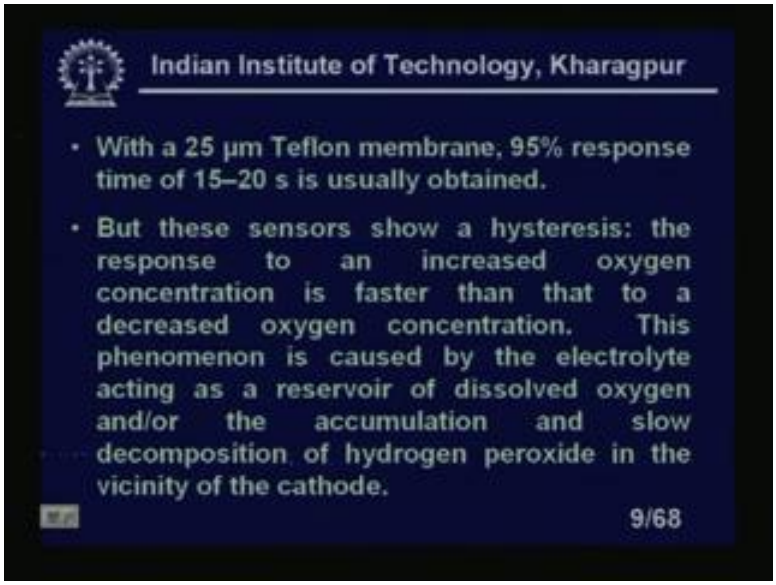

With a 25 micron Teflon membrane 95 percent, response time of 50 to 20 seconds see usually, obtained right. Response time means, if it is a within 50 or 20 seconds, if you a step input suddenly, that suppose a probe is inserted or there is a change in the concentrations of dissolve oxygen or partial pressure of the oxygen. So, if we use a 25 micron Teflon. So, 90 percent response time is usually, obtained right, of 20, 15 to 20 seconds you will obtain. But these sensors show a hysteresis the response to an increased oxygen concentration is faster than that to a decreased oxygen concentration.

Step change if basically, response time varies depending on the direction of the step change in oxygen concentration. Suppose I had, because it is very unusual though I

mean, it is oxygen concentration or oxygen partial does not very rapidly, but there suppose there is a change suppose. So, that is what I am saying? That there is some sort of hysteresis in the systems, but the sensor shows a hysteresis, that is means, that the response to increased oxygen concentrations will be different when the this, when the when we are decreasing the concentration. This phenomena is caused by the electrolyte acting as a reservoir of dissolved oxygen or the accumulations and slow decompositions of hydrogen per oxide in the vicinity of the cathode.

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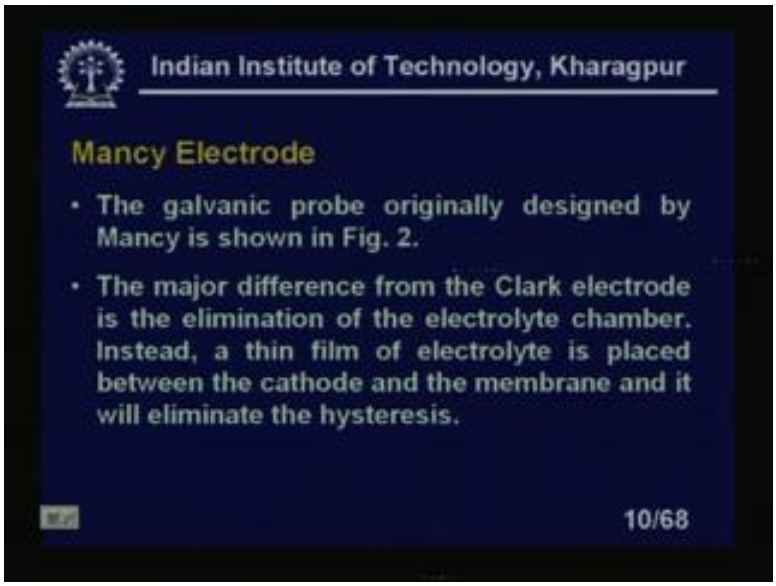

Mancy electrode; the galvanic probe originally, designed by the Mancy shown in figure 2 the major difference. From the Clark electrode is the elimination the electrolyte chamber; instead a thin film of electrolyte is placed, between the cathode and the membrane. And it will eliminate the hysteresis, hysteresis the problem; that means increased concentrations. And decreased concentrations, it will be a I mean, giving a problem. So, that type of problem can be eliminated in the Mancy electrode right.

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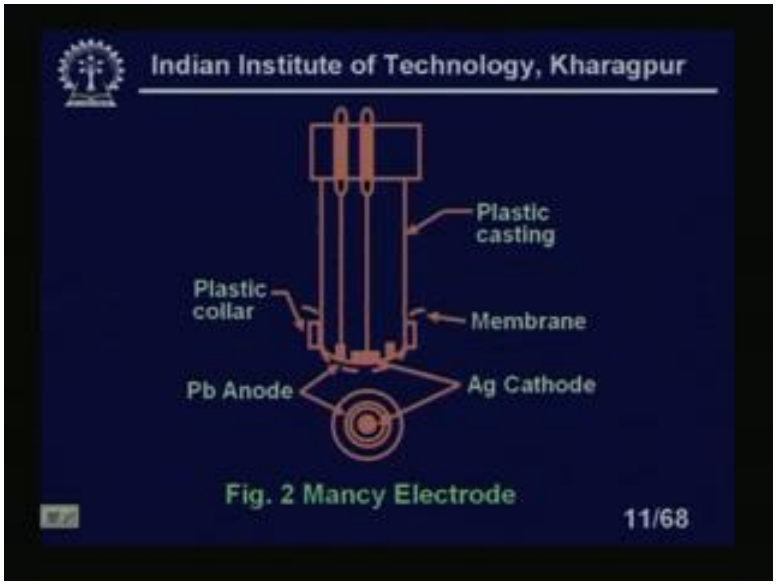

So, this is our Many electrodes, we can see here plastic casting is there the membrane is there, an A g cathode we have a P b a lead anode and plastic collar, this you can see here. Due to relatively, large chamber point 6 centimeter cathode, employed a micro ammeter could be directly connected to the probe. We do not need further, amplification and improved probe stability was reported compared with the earlier polarographic probes. But the useful probe, life may be somewhat restricted, because the available surface area of the anode is relatively small. So, this is another problem anode surface is gradually, oxidized with the use until the probe ceases to function. So, it will be oxidized until the probe ceases to function.

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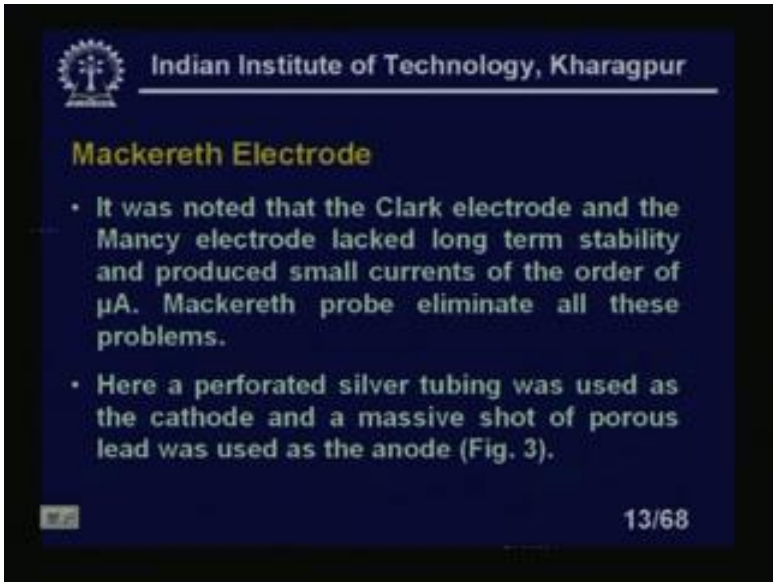

Mackereth electrode, it looks like this it was noted that the Clark electrode and the Mancy electrode lacked long term, stability as I told you, because of the depositions and all those things. So, because in the case of Clark electrode, we have to clean it all those things are there whereas, here there is a deposition in the case of Mancy electrode. So, this type of thing will be not there in the case of Mackereth electrode, it was noted that the Clark electrode and the Mancy electrode, lacked long term stability. And produce small currents of the order of microampere, we have seen that the current is quite small, Mackereth probe eliminate all this problems. Here perforated silver tubing was used as a cathode and a massive shot of porous lead was used as anode figure 3.

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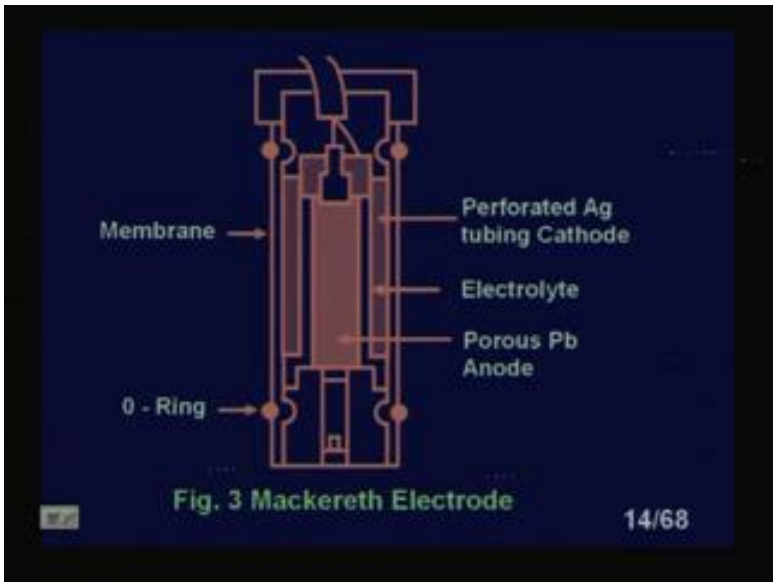

Porous P b lead is anode and this is electrolyte, you can see, we have o ring and perforated tubing cathode. So, this is our Mackereth electrode, you can see here, here O Ring and membrane is there.

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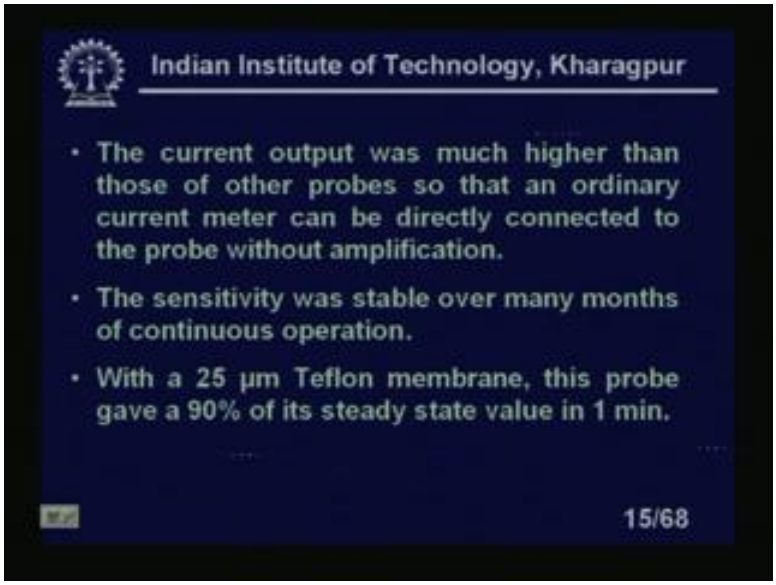

The current output was much higher than those of the other probe. So, that an ordinary current meter can be directly connected to the probe without amplification this is very important because; obviously, any entity will find it is corrupted with noise. So, that if the current output is large. So, all, this problem signals noise ratio will be quite good. So, we do not need any further amplification, the sensitivity was stable over many months of continuous operation, this is again a very important thing in the case of electrode design. With a 25 micron Teflon membrane, this probe giving 90 percent of its steady, state value in 1 minute. So, it is a quite fast not that, fast compared to the Clark or electrode, but as I told, you that response time, fast is not very stringent requirement or a very rigid requirement for bio reaction. So, in that our application, this probe can be nicely, used most important thing, it can be used over a longer period, without any calibrations or recleaning.

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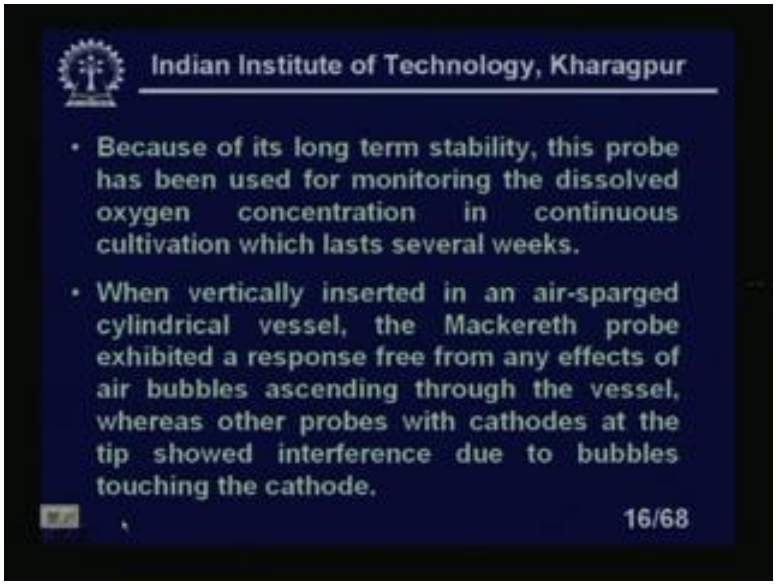

Because of it is long term stability, this probe has been used for monitoring the dissolved oxygen concentration in continuous cultivation, which lasts several weeks in some cases, I said 72 hours in some cases, it is can be continue over a week. So, in that type of situation, this electrode is very much suitable, though the response time is very. I mean, is quite bad, I should say which does not matter, because I will not sample, I will not measure every minutes.

I may measure every hour, because of if the with reaction going on several weeks; obviously, just reading in half an hour of the dissolved oxygen concentration will suffice when vertically, inserted in a air-sparged cylinder vessel. The Mackereth probe exhibited a response free, from any effects of air bubbles, ascending through the vessel which is very obvious in many situation. We will find whereas, other probes, because this type of situation will arise in the air column, column bioreactor. So, bubble column, if you know that a basic principle is something like this that it is like this.

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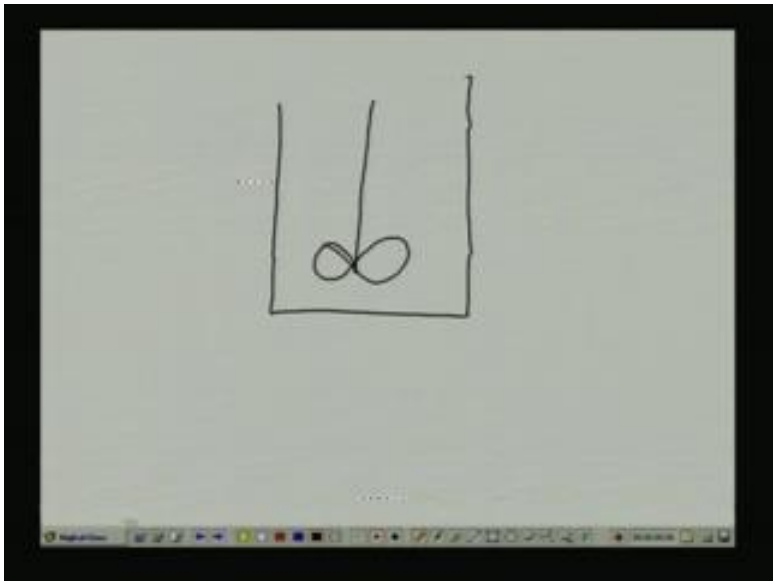

I have, so dissolved oxygens are, because instead of suppose I have a stirred tank reactors here. So, it is rotating and oxygens are getting dissolved, in the case of bubble column reactors, what will happen sorry what will happen?

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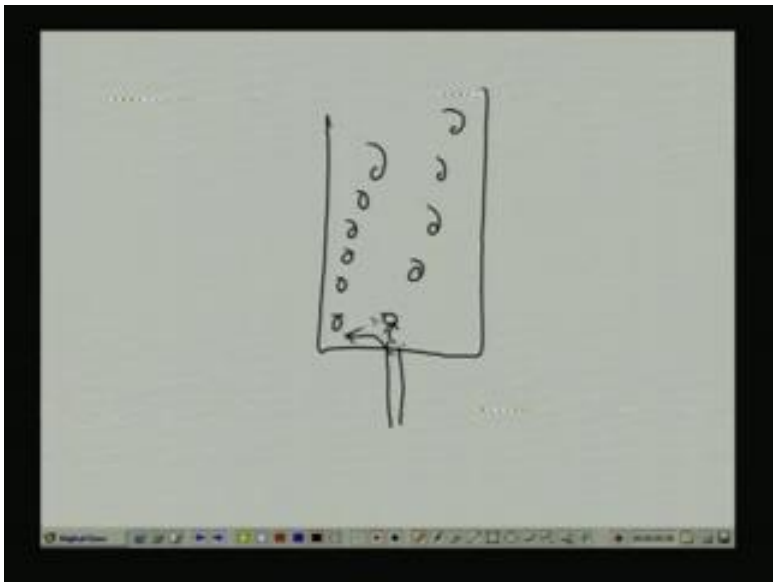

That I have a vessels and I am purging, oxygen through this one. So, bubble will go out, like this one, it will go the air bubble will go. So, it will purge along this one. So, this type of this may cause problem in other type of dissolve oxygen probe, it will not make a problem in this probe. Let us go back when vertically, inserted in an air spurged cylinder vessel the Mackereth probe exhibited response free from any effects of air bubbles.

Because the function of the air bubbles to increase the dissolved oxygen concentrations or partial pressure of the oxygens in the bulk medium of the liquid where the actually my reaction takes place right, where the other probes in this case. So, that is the most important thing which we should consider that problem does not arise and if you use a Mackereth electrode. So, the Mackereth probe exhibited response free from any effects, of the air bubbles ascending through the vessel whereas, other probes with cathodes at the tip showed interference due to bubbles touching the cathode. So, this is again problem in other.

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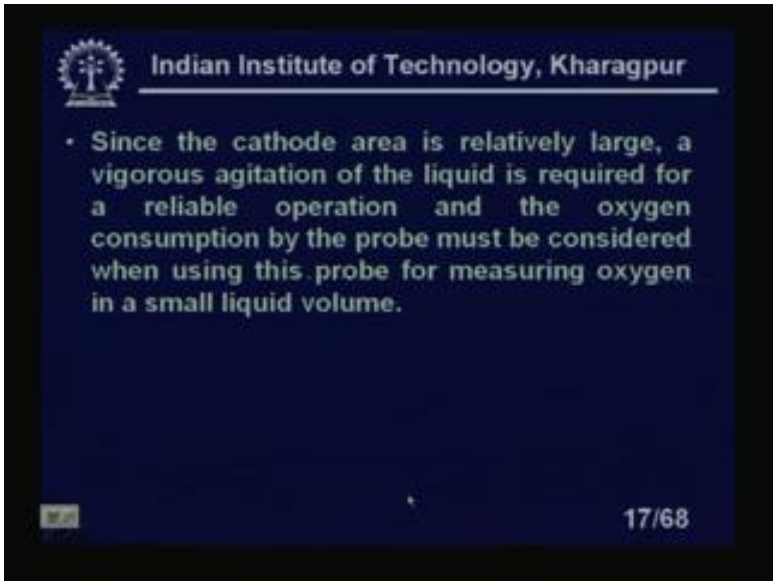

Since the cathode area is relatively, large a vigorous agitations of the liquid is required for reliable operations, because since the cathode area is large so; obviously, it should average. So, the vigorous agitations of the liquid is required for reliable operations and oxygen consumption by the probe must be using the probe for the measuring oxygen in a small liquid volume. So, it is; obviously, if we use a c s t r continuous stirred tank reactor; obviously, the liquid will be vigorous only, problem this condition will not be satisfied, if you make a very gentle I mean rotations of the blades.

So, that the a very sensitive, I mean, culture like animal cell and all those things, So, this question arises. Otherwise for most of the conditions like the reactions, where the you we are using c s t r continues stirred tank reactors. So, this type of problem does not, I mean arise. So, this type of condition will always will be there, because it is rotating at a high speed so; obviously, there is a vigorous agitations of the bulk medium or the liquid. The

probe may not be suitable for a viscous medium, if the viscous the liquid this is having the problem, because you use the bio-reaction the viscosity does not remain same at initial stage. When the reaction start is the viscosity, will be less as the reaction going on for an example, very trivial things I am talking about the yeast growth. You will find that the you will find that as the reaction goes by at the end of the day, you will find that the liquid becomes very much viscous.

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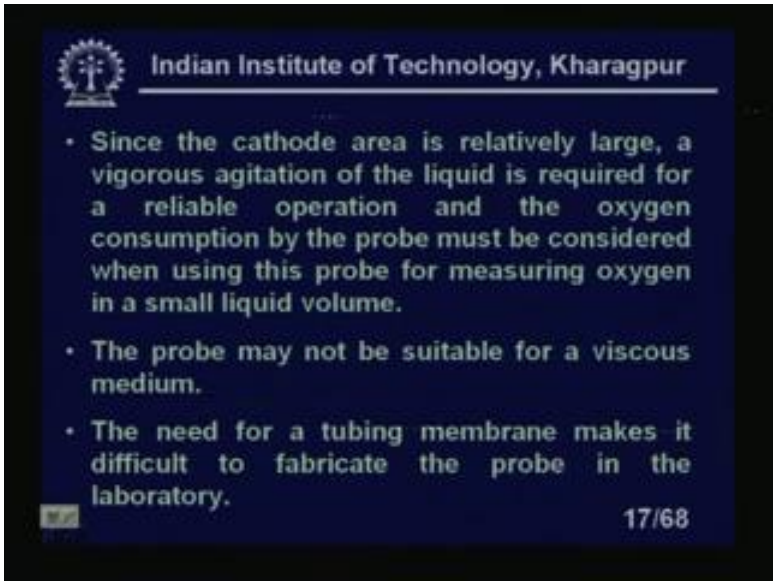

So, need for a tubing membrane makes, it difficult to fabricate the probe in the laboratory this is another problem, which is like in the Clarke electrodes is very simple to make.

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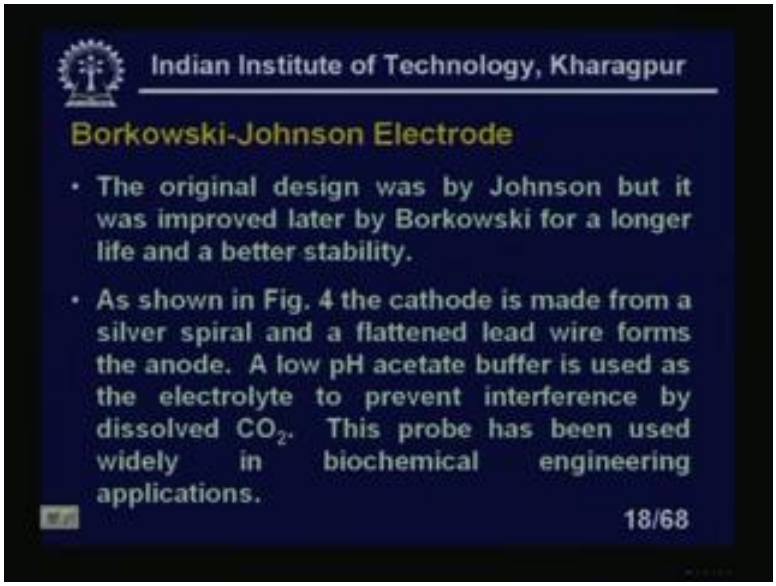

Borkowski and Johnson electrode: The original design was by Johnson, but it was improved later by Borkowski for a longer life and better stability, as shown in figure 4. The cathode is made from a silver spiral and a flattened, lead wire forms the anode a low p h acetate, buffer is used as a electrolyte to prevent interference by the dissolved carbon dioxide. This probe has been used widely in the biochemical engineering applications.

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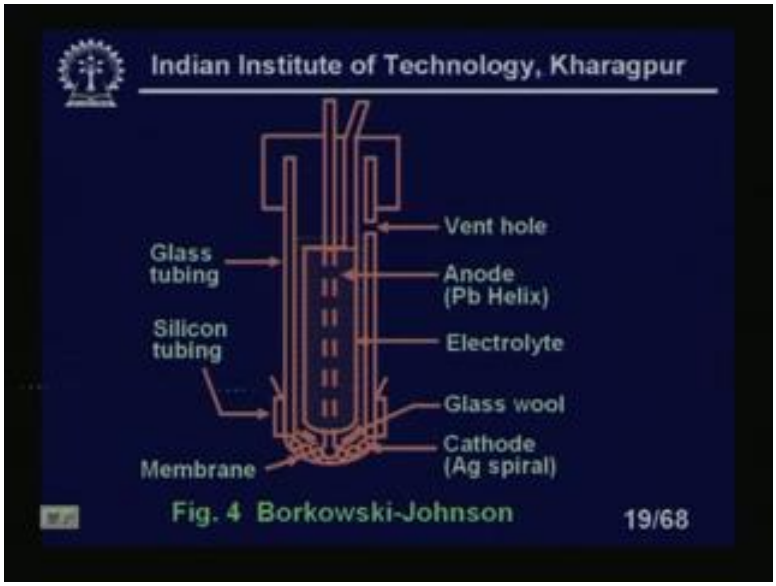

You see here, we have a glass tubing anode is there which is helix, then we have electrolyte. We have a glass wool, there a cathode which is I mean, silver spiral sorry and we have a membrane silicon tubing is there. So, this is our glass tubing and 2 2 wires are coming out.

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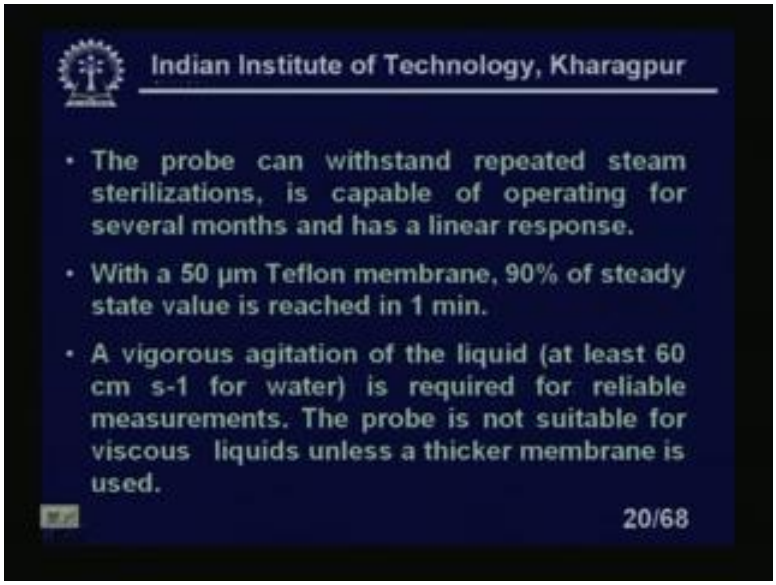

The probe can be withstand repeated steam sterilization and is capable of operating for a several months as a linear response, with a 50 micron Teflon membrane 90 percent of steady state value is reached in 1 minute. This is almost same as the previous electrode, electrode a vigorous agitations of the liquid at least 60 centimeter per second for water. Velocity rotational velocity, if you take is required for reliable measurement the probe is not suitable of viscous liquids unless, thicker membrane is used same as the previous electrode.

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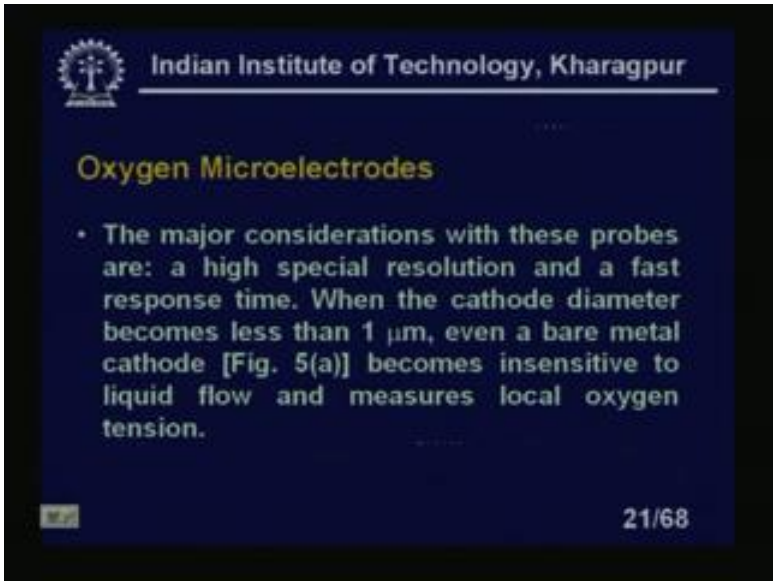

Oxygen microelectrodes the major consideration with these probes are a high special resolution and a fast response time, because in if I in some conditions, we may need a fast response. So, that type of that type of cases 1 minute or even 20 seconds is might not be I mean very desirable properties, we have to reduce that. So, that we can do in this type of oxygen then as it is name incline implies, it is a very small in size high special resolutions. And a fast response time, when the cathode diameter becomes, less than one micrometer even a bare metal cathode, which is figure 5 a becomes insensitive to liquid flow and the measures local oxygen tension tensions or oxygen concentration, it is almost the same thing.

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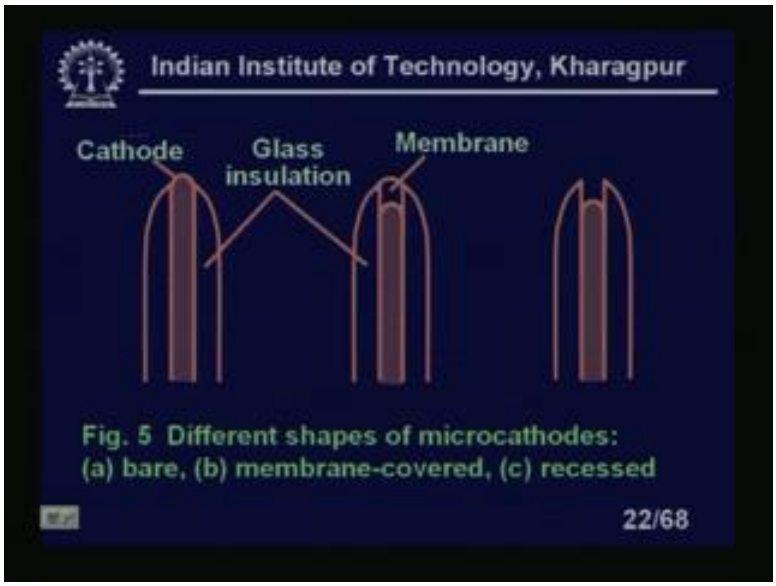

You can see here, so 5 a b c all these are this is a bare this is glass insulation. This is a cathode, this is a membrane, and this is like this one recessed membrane covered and recessed 3 difference we have shown.

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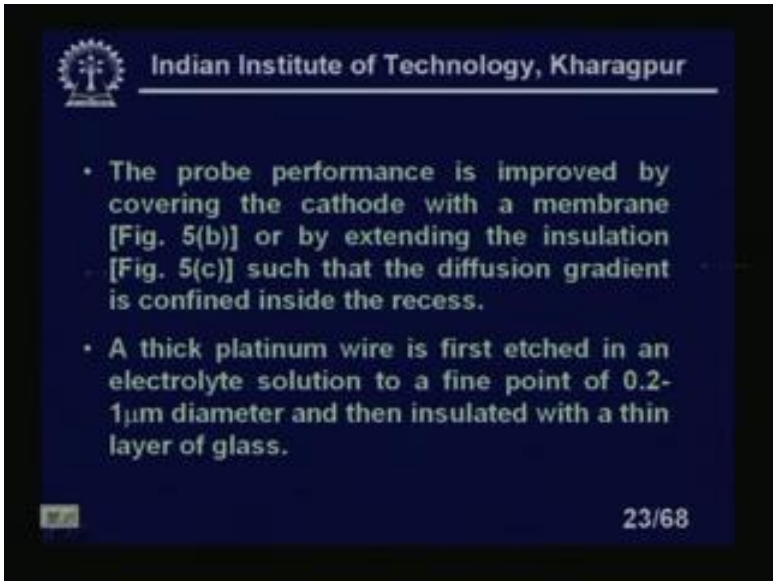

The probe performance is improved by covering the cathode with a membrane; obviously, if I cover my membrane. So, it will be it is possibly, slower and by extending the insulation such that in shown in figure 5 c diffusion gradient is confined inside the recess. A thick platinum wire is first etched in an electrolyte solution to a fine point of point 2 2 1 micrometer diameter. Then insulated with a thin layer of glass right, I will repeat a thick platinum wire is first etched in an electrolyte solution to a fine point of point 2 2 1 micrometer diameter and then insulated with a thin layer of glass.

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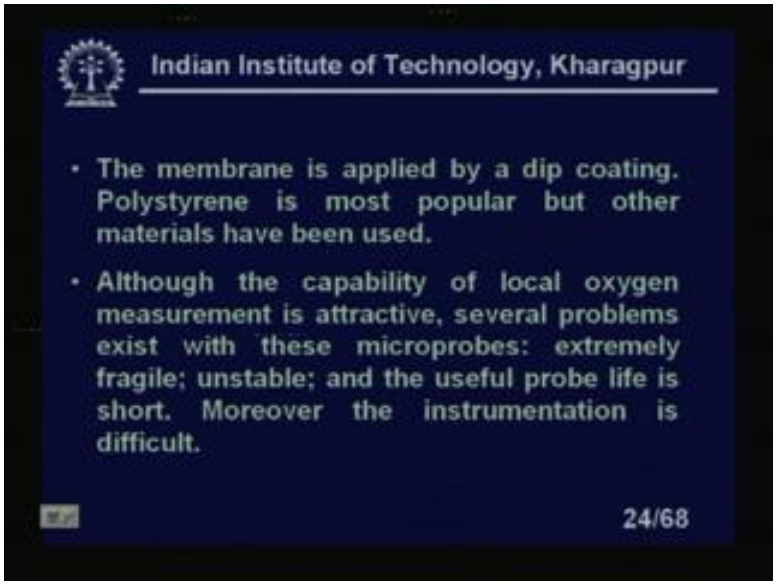

The membrane is applied by a dip coating, polystyrene is most popular, but other materials have been also used. Although, the, of the local oxygen measurements is attractive, several problems exist with these microprobes extremely unstable. Useful probe life is short moreover the instrumentation is difficult. Repeatability of the sensor is poor each and every sensory is to be calibrated separately. So, all these problems are there. Now, electrode metals, what type of metals? We will use in the electrodes, we will cover 1 by 1 membrane type of electrolytes. We are using all this thing, and finally some instrumentation.

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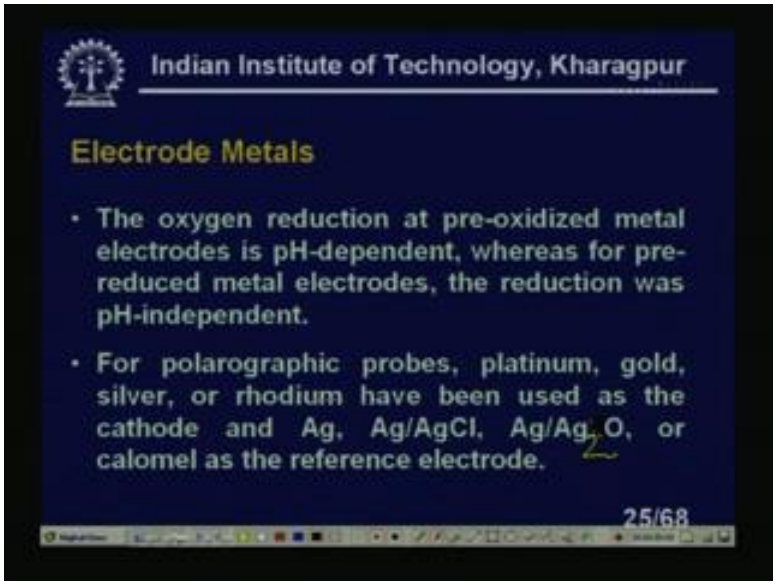

The oxygen reduction at pre-oxidized metal electrode is a p H dependent, where as for pre-reduced metal electrodes the reduction was p H independent. For polarographic probes, platinum gold silver and or rhodium have been used as a cathode and silver and silver silver chloride, silver silver dioxide. This A g 2 O please note, it is not A g 2 it is A g 2 will be in subscript. So, it is like this, so it will be 2 O sorry 2 O. So, I can or calomel as a reference electrode is used.

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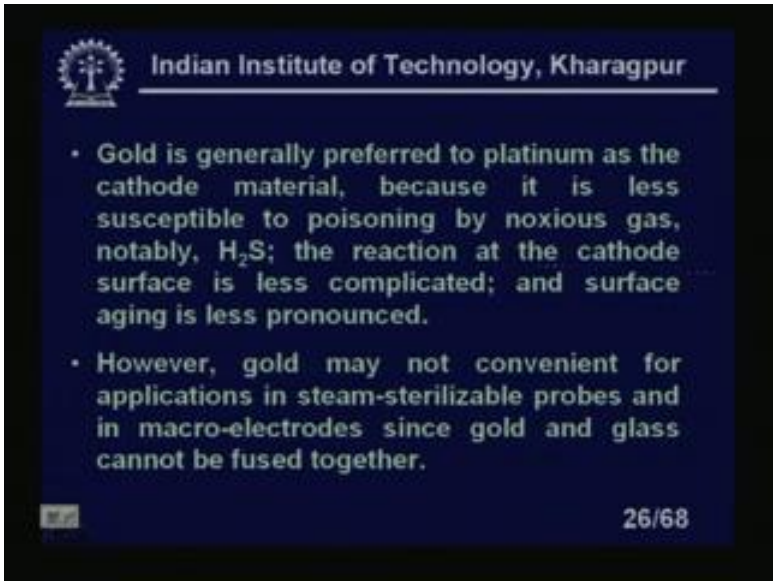

Gold is generally preferred to platinum as the cathode material, because it is less susceptible to poisoning by noxious gases notably H 2 S hydrogen sulphide. And the reaction at the cathode surface is less complicated and the surface aging is less pronounced. However gold may not convenient, for application in steam-sterilizable probes the macro-electrodes, since gold and glass cannot be fused together. So, it is a larger I mean, I mean type of electrodes. So, it is if I want to make steam sterilizable that is not a very suitable for this type of purposes.

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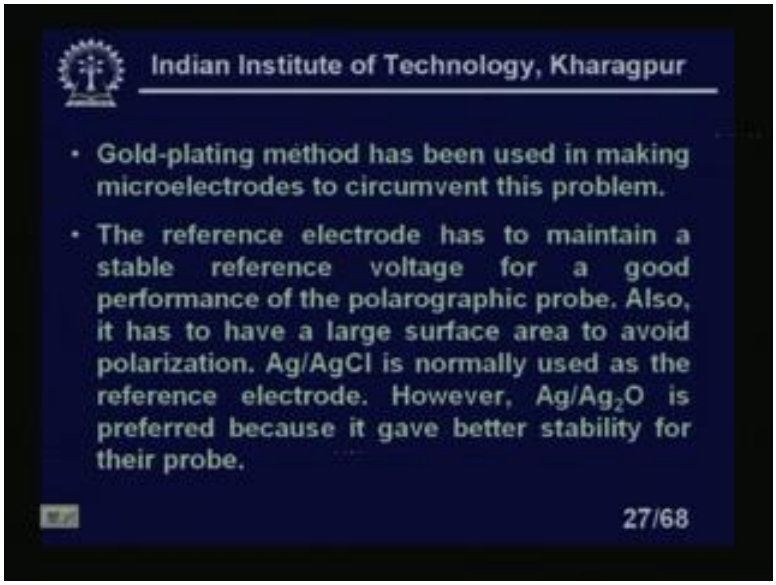

Gold plating method has been used in making the microelectrodes to circum, circumvent these problems, so that if it is a macro electrode, it is not possible, but microelectrode it is possible. The reference electrode has a, has to maintain a stable reference voltage for a good performance of the polarographic probe also, it has to have a large surface area to avoid polarizations. So, the surface area should be large, silver silver chloride is normally, used as a reference electrode. However silver silver dioxide is preferred, because it gave better stability for their probe.

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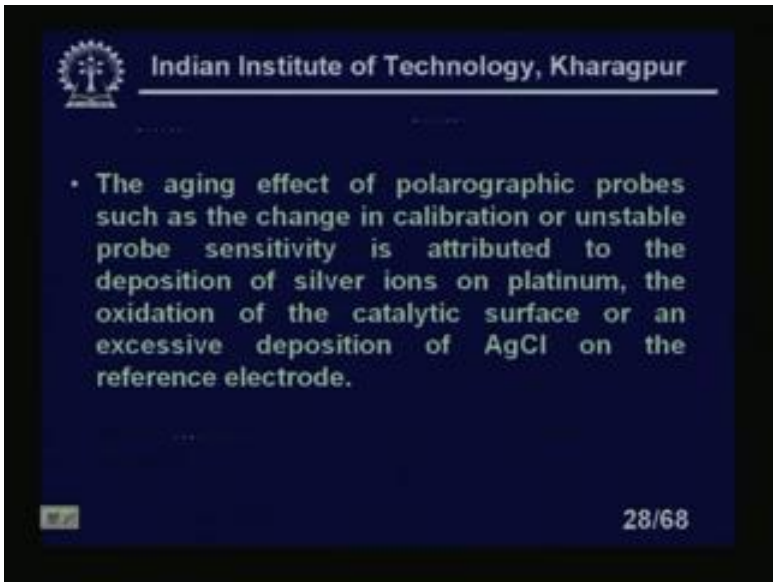

The aging effect of the probes, such as the change in calibrations or unstable probe sensitivity is attributed to the depositions of silver ions on platinum, and the oxidations of the catalytic surface or an excessive deposition of silver chloride on the reference electrode.

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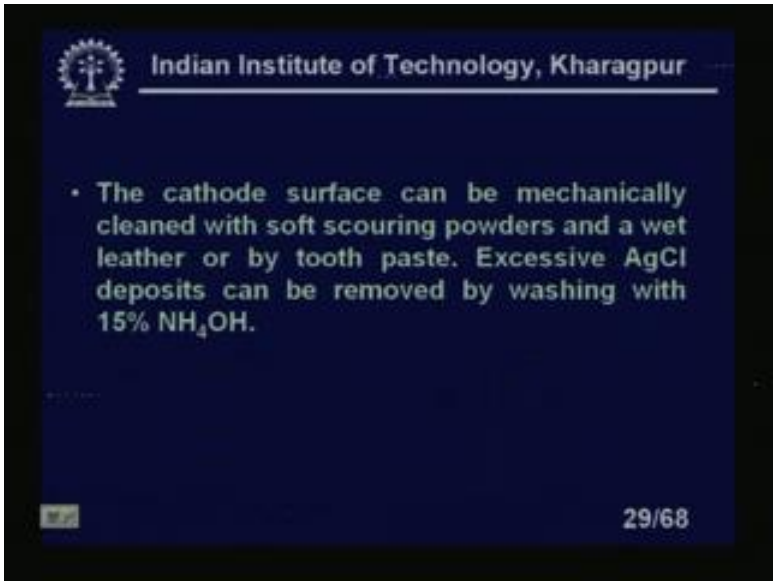

The cathode surface can be mechanically, cleaned with soft scouring powders. So, if you regularly, clean it with a cleaning powders and wet leather or by tooth paste. So, excessive silver chloride deposits can be removed by washing with sodium. I mean, ammonium hydroxide 15 percent ammonium hydroxide is possible. This I told you from the very beginning, where we were at cleaning of the electrodes.

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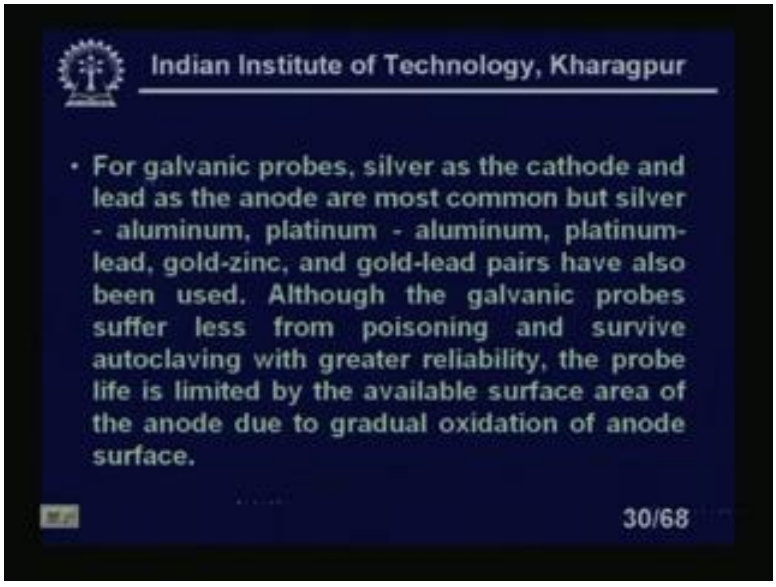

For galvanic probes the silver as the cathode and lead as the anode are most common. But sliver aluminum platinum aluminium platinum lead gold gold lead pairs have also been used although the galvanic probes suffered less from poisoning and survive

autoclaving with greater reliability. The probe life is limited by the available surface area, of the anode due to gradual oxidations of the anode surface, this is again problem.

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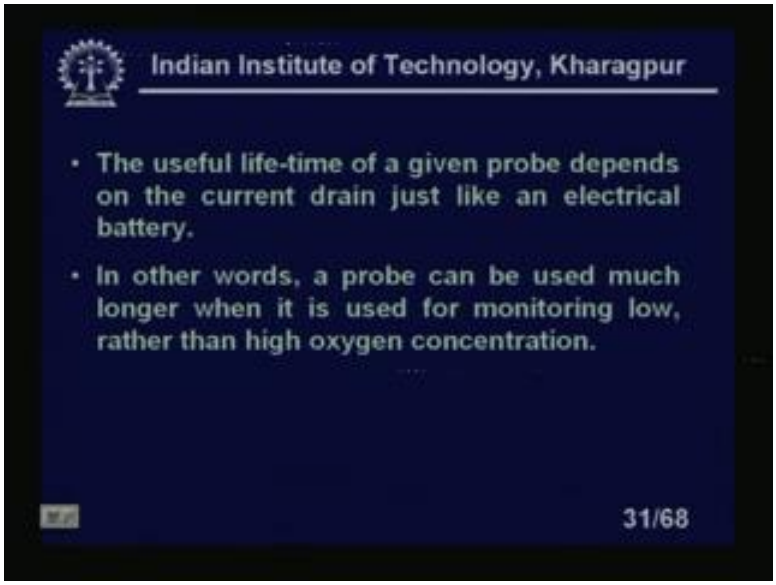

The useful life-time of given probe depends on the current drain, just like an electrical battery in other words a probe can be used much longer. When it is used for monitoring low rather, than the high oxygen concentration this is not in our hand. So, it varies suppose in a reactions, because in many reactions in bio process we have seen that, you see the many concentration. We cannot measure online, suppose a substance concentration I mean, C l concentrations we cannot measure only the D O 2. We can measure and that will give you the, suppose when the D O 2 is initially, is when it the reactions start. Its starts we find that the D O 2 is not growing that fast; that means, the whatever the D O 2 that we are supplying that is consumed by the cells.

At the end of the reactions, after few I mean, several hours or might be several days, we will find that no more oxygens are getting consumed due to concentration is increased. But coming to a steady state; that means, you can see that whatever oxygen, which we are supplying, it is getting consumed and after that is if it is if it is further. So, due to again, we will find that the it will indicate that the cell reaction is completing, it is time to take out the cell from our or take out the product. So, due to concentration measurement is very important right. So, I mean, and it is varying, so that I mean, it is not in our hand, but in some condition. Where we have just monitor not much of control that is what is the value of the D O 2 in what are the safe level of D O 2 in the oxygen.

Suppose in the marine, I mean animals will need the measure the D O 2 concentrations there. So, in that type of situations, we can say that the we can either low monitoring or high monitoring, but it is not in our hand.

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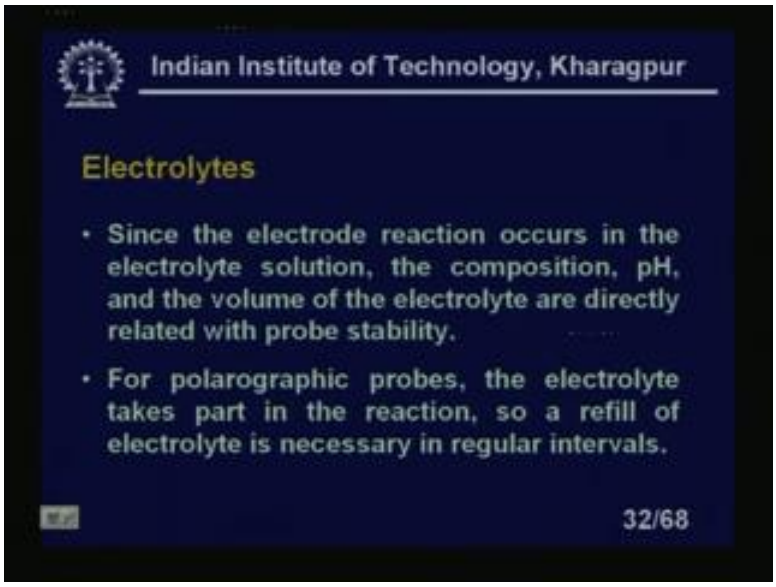

Electrolytes since the electrode reactions, occurs in the electrolyte solution the composition comma p H and the volume of the electrolytes are directly related to the probe stability. For polarographic probes the electrolyte takes part in the reaction, so a refill of electrolyte is necessary in the regular intervals. This is a very important thing is very difficult so that what we have to do? A, we have to use a reservoir, we will discuss in the next slide.

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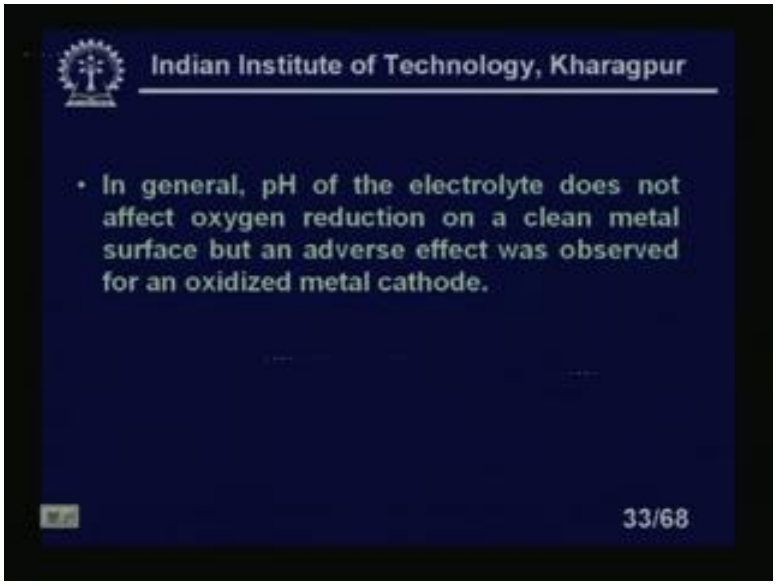

In general pH of the electrolyte, does not affect oxygen reduction on a clean metal surface, but an adverse effect was observed for an oxidized metal cathode.

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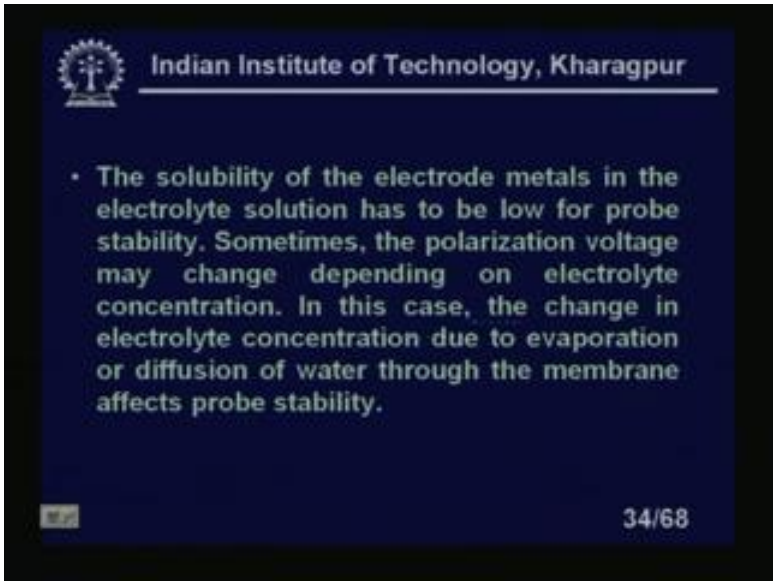

The solubility of the electrode metals in the electrolyte solution has to be low for probe stability, sometimes the polarization voltage may change the depend, change depending on the electrolyte concentration. In this case the change in electrolyte concentration due to evaporation or diffusion of water through the membrane affects probe stability. Because any liquid you will find, when you will make the reactions and mostly it is in

water. So, water may diffuse through the membrane. So, that will again change the properties of the electrolyte.

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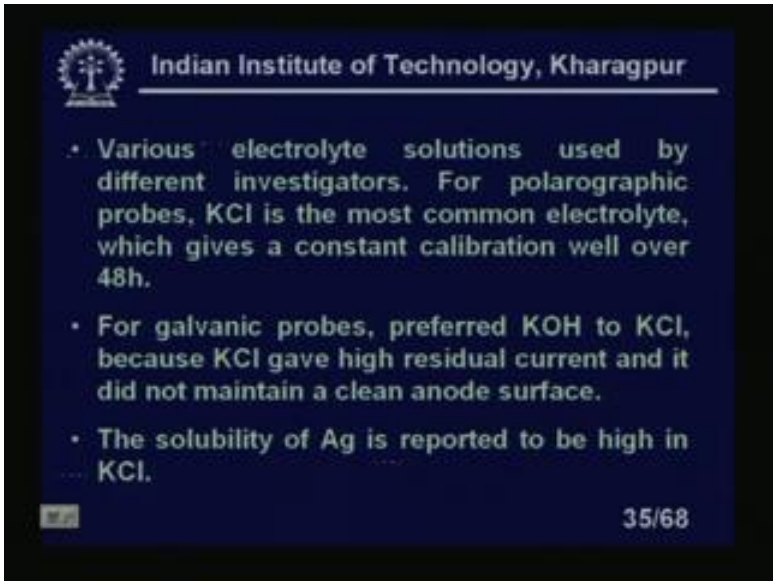

Various electrolyte solution used various electrolyte solution used by different investigators for polarographic probes. Potassium chloride is the most common electrolyte, which gives a constant calibration well over 48 hours, which is quite for many of the applications for galvanic probes, preferred potassium hydroxide than the potassium chloride. Because potassium chloride gave a high residual current and it did not maintain a clean anode surface. The solubility of silver is reported to be high in K C l solution.

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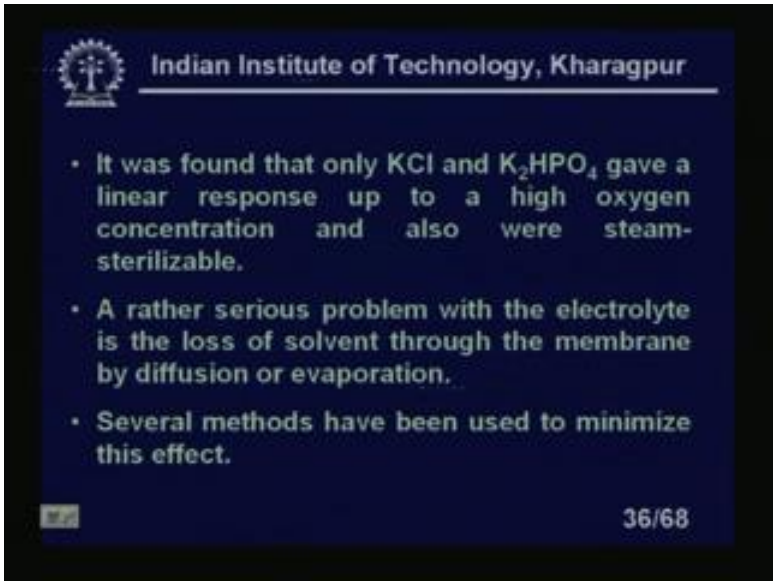

It was found that only K C l and K 2 H P O 4 gave a linear response up to a high oxygen concentrations and also where steam sterilizable right. So, they gained steam sterilize sterilizable is a good property and also autoclaving is a good property of the system. That is also always, we have to think about, because the contamination is a great problem in may all the reactions. We will find especially, when you are using the bioreactors, if we are using the field that is does not matter, because many reaction does not allow a little I mean, contamination that is to be, we have to think that in mind. Rather serious problem with the electrolyte is a loss of solvent through the membrane by diffusions or evaporation several methods, have been used to minimize this effect.

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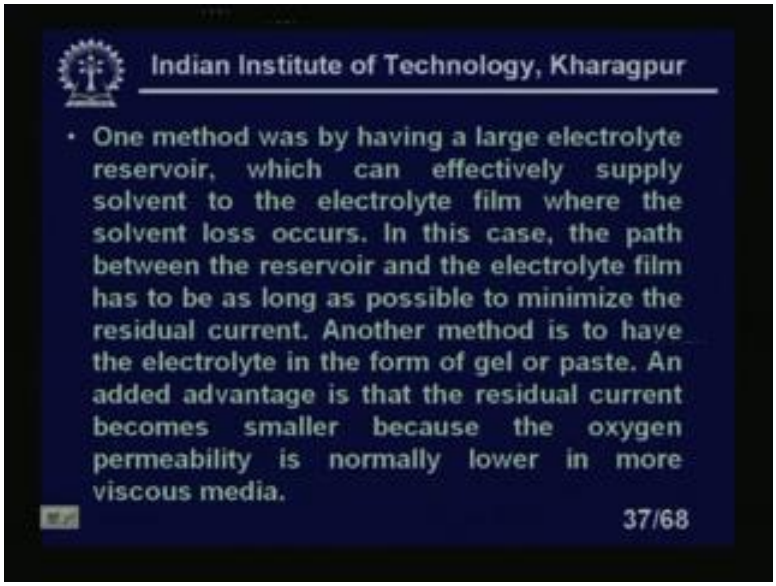

One method; by having a large electrolyte reservoir as I told you which can effectively supply solvent to the electrolyte film where the solvent loss occurs. In this case the path between the reservoir and the electrolyte film has to be as long as possible to minimize, the residual current. Another method is to have electrolyte in the form of gel or paste and added advantage is that the residual current becomes smaller, because the oxygen permeability is normally, lower in more viscous medium.

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Recent development has been in the use of a solid electrolyte instead of the conventional liquid forms, this all will eliminate through the previous problems, which we have discussed.

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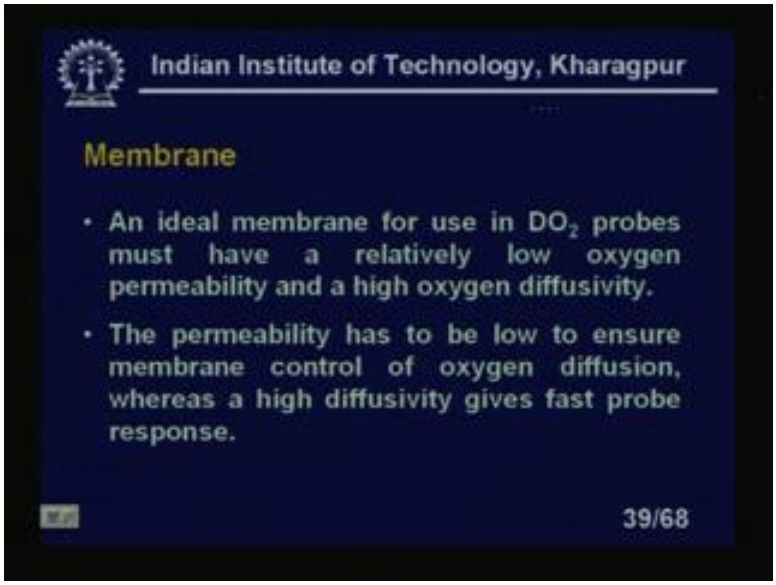

Membrane: an ideal membrane for use in D O 2 probes must have a relatively, low oxygen permeability, high oxygen diffusivity. The permeability has to be low to ensure the membrane control of the oxygen diffusion whereas, the high diffusivity gives a fast probe response, so you have to make a compromise.

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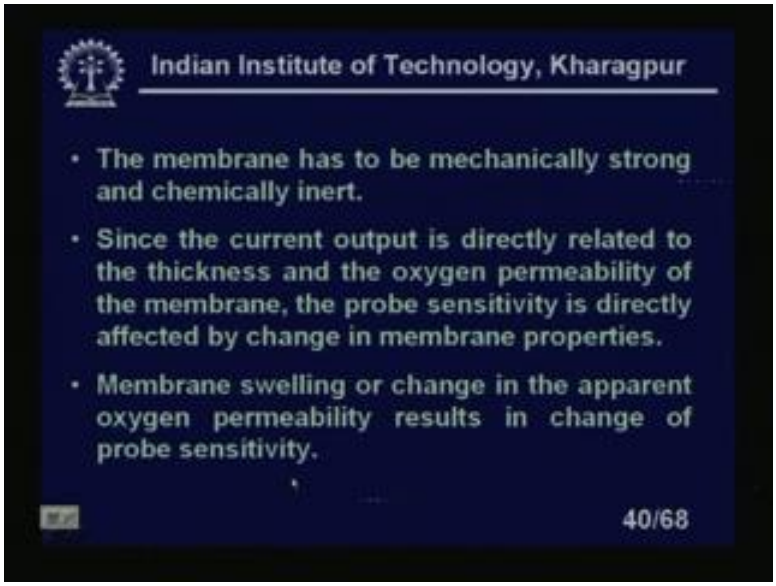

The membrane has to be mechanically, strong and chemically, inert right; that means, mechanically strong means; it can, should withstand the high pressure. It can should I mean, in a position to withstand high temperature at least 120 degree centigrade. Little more than 1 atmosphere, it is to be I mean, because if you do for autoclaving. So, this I

mean, high temperature high pressure, conditions have to be satisfied. Since the current output is directly related to the thickness and the oxygen permeability, of the membrane. The probe sensitivity is directly, affected by the change in the membrane properties. Membrane swelling or change in the apparent permeability, results in the change of probe sensitivity, sometimes membrane swells, if it lies over a long time in a liquid. So, that will change the apparent oxygen, this is not a problem. We have to recalibrate or we have to change the membrane that is it there is no other solution.

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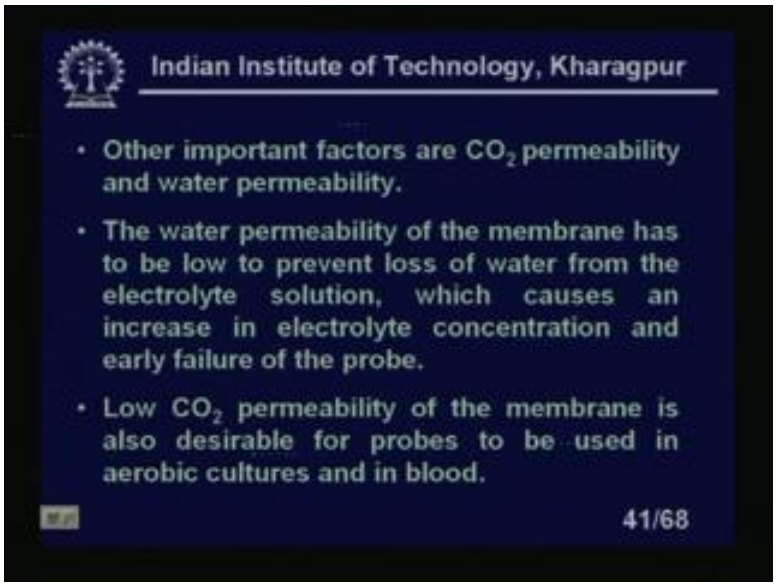

Other important factors are C O 2 permeability, and water permeability the water permeability, of the membrane has to be low to prevent loss of water from the electrolyte solution, which causes an increase in the electrolyte concentrations. And early failure of the probe low C O 2 permeability of the membrane is also desirable for probes to be used in aerobic cultures. And in blood sometimes, under the means, of oxygen concentrations and that is also important.

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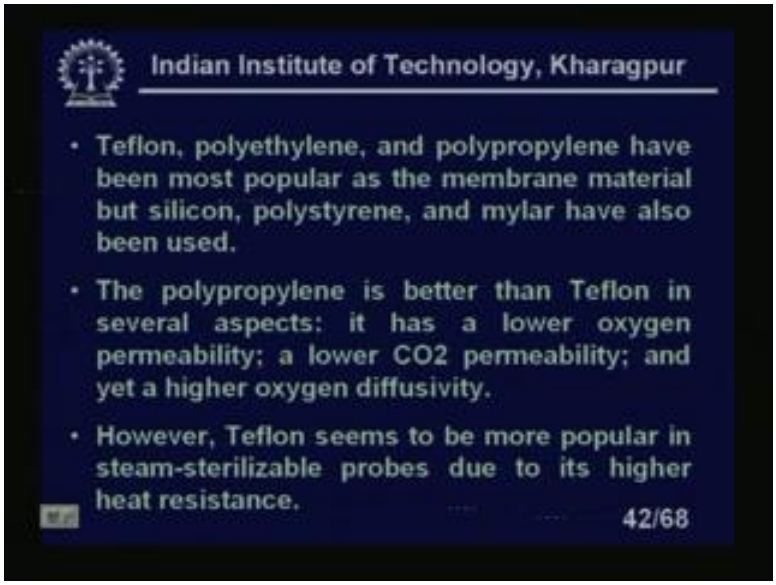

Now, the material, what are the different materials used for the making the membrane? Really I will just I will say, that Teflon is the mostly, widely used material for making the membrane Teflon. Polyethylene have been most popular as the membrane material, but silicon polystyrene and Mylar have also been used, but still I should say that Teflon is the most widely, used membrane for making D O 2 probe. The polypropylene is better than the Teflon in several aspect. It has a lower oxygen, permeability a lower carbon dioxide permeability and yet a higher oxygen diffusivity. However Teflon seems to be more popular in a steam sterilizable probes due to the higher heat resistance that I told you earlier. So, this is the property which must have.

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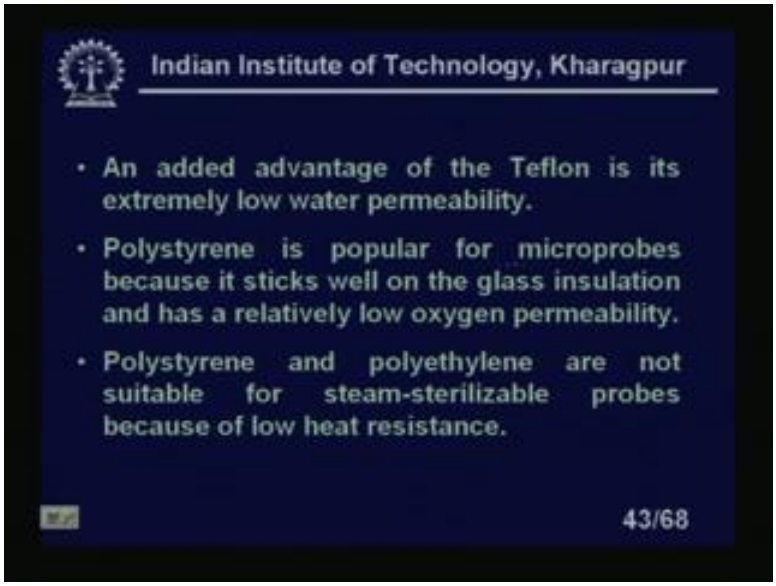

An added advantage of the teflon is, it is extremely, low water permeability, so this is another advantage of the teflon. Polystyrene is popular for microprobes, because it sticks well on the glass insulation and has a relatively, low oxygen permeability. Polystyrene and polyethylene are not suitable for steam sterilizable probes, because of low heat resistance. So, the problem is there on one side is a low oxygen permeability and the other side it has a low heat resistance.

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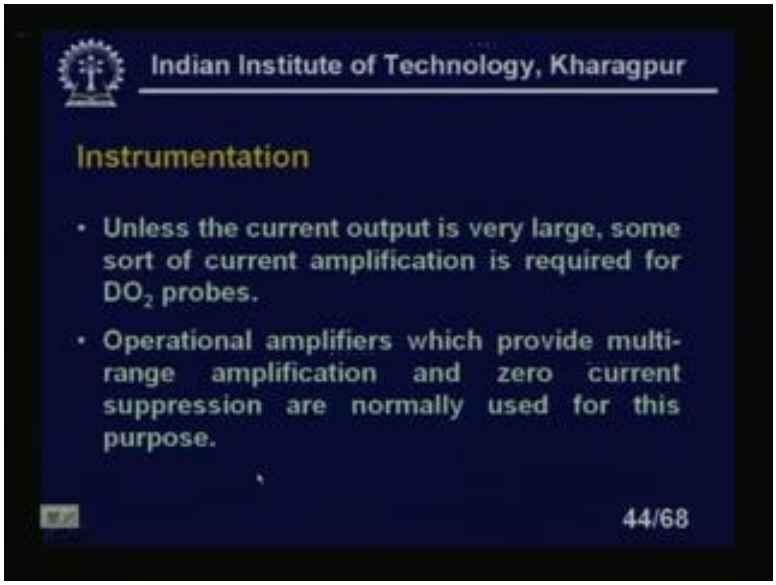

Instrumentation: let us look at… Unless the current output is very large, some sort of current amplifications is required for D O 2 probes. So, we know various types of current amplification that, single condition is we can do, it has improved a lot. So, that is not a problem, operational amplifiers, which provide multi-range amplifications and current suppression are normally, used for this purpose.

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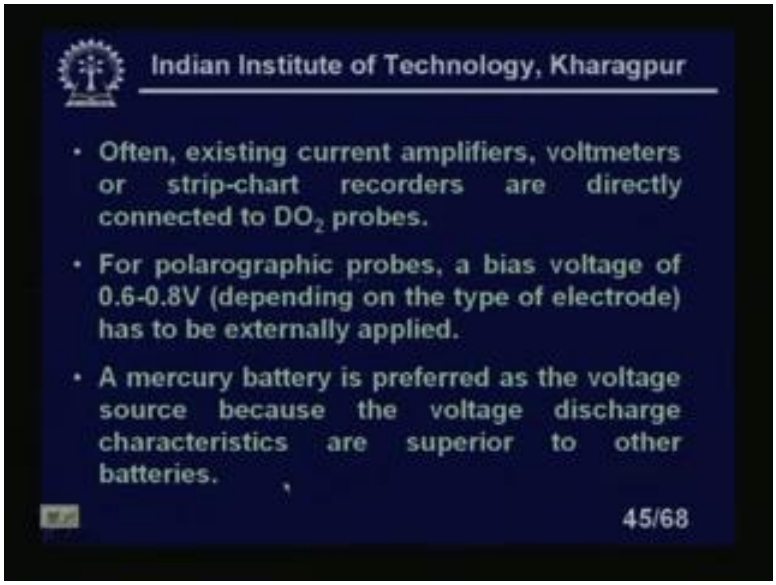

Often, existing current amplifiers, voltmeters or strip chart recorders are directly, connected to D O 2 probes. Obviously, one thing where may not mentioned, that you see any D O 2 probe must be any D O 2 probes, must be appended by a; obviously, by the followed. I should say followed by a by a current transmitter, because the current amount of current, you will get there is directly from the probe is not sufficient to be transmitted this is not sufficient, so we have to use some current transmitter. So, that it will go to the computer right. We can monitor their itself, whatever the current we will get that sufficient for monitoring, but for control purpose.

If I have to send to the computer, I have to use some current transmitter there itself. So, any probe must be with a followed by current transmitter for polarographic probes a bias voltage of 0.6 to 8 volt depending on the type of electrodes has to be externally applied. That we have seen always, we need a bias voltage, which usually lies between 0.6 to 0.8 volt. A mercury battery is preferred as the voltage source, because the voltage discharge characteristics are superior to other batteries.

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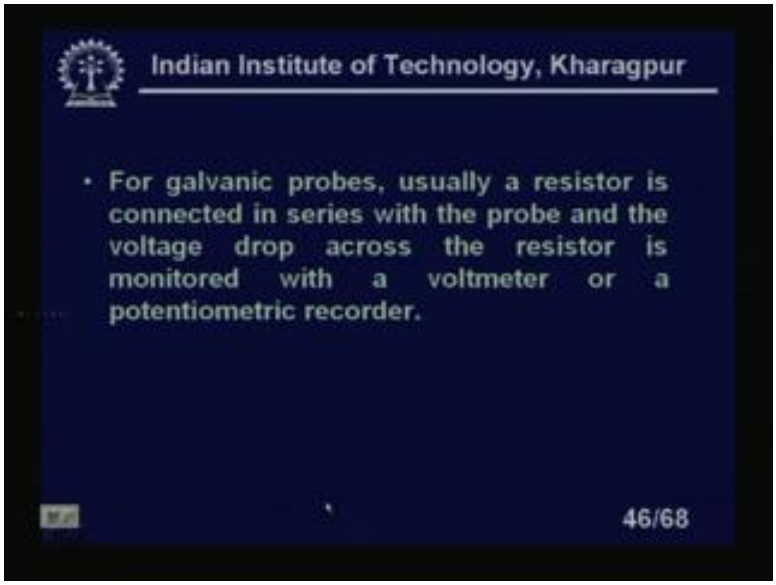

For galvanic probes, usually a resistor is connected in series with the probe and the voltage drop across the resistor is monitored with a voltmeter or a potentiometric recorder.

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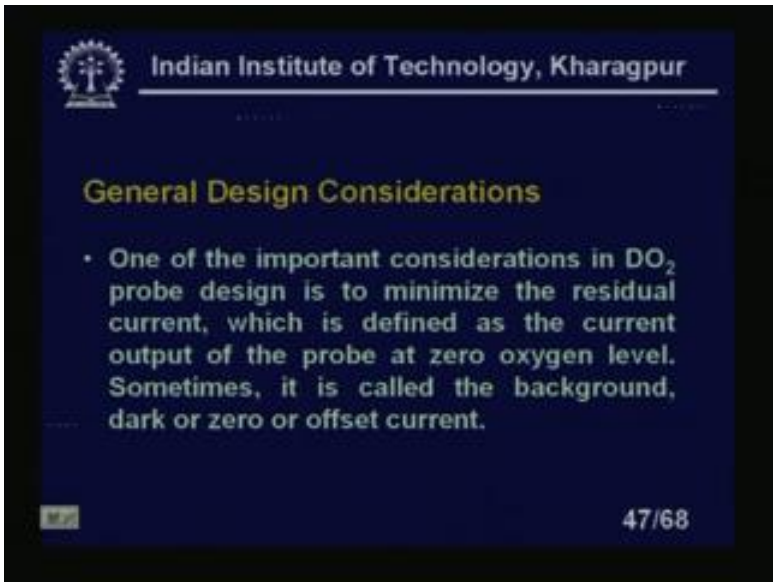

Now, general design considerations if I look at one of the important considerations in D O 2 probe design is to minimize the residual current which is defined as the current output of the probe at 0 oxygen level that is when there is no level. But you may immediately ask the question how will you know that is a 0 oxygen oxygen concentration in the bulk liquid is 0. We will show that thing how you can make it 0

sometimes it is called the background dark or zero or offset current. I should say the background current I should say the dark current that is more appropriate name.

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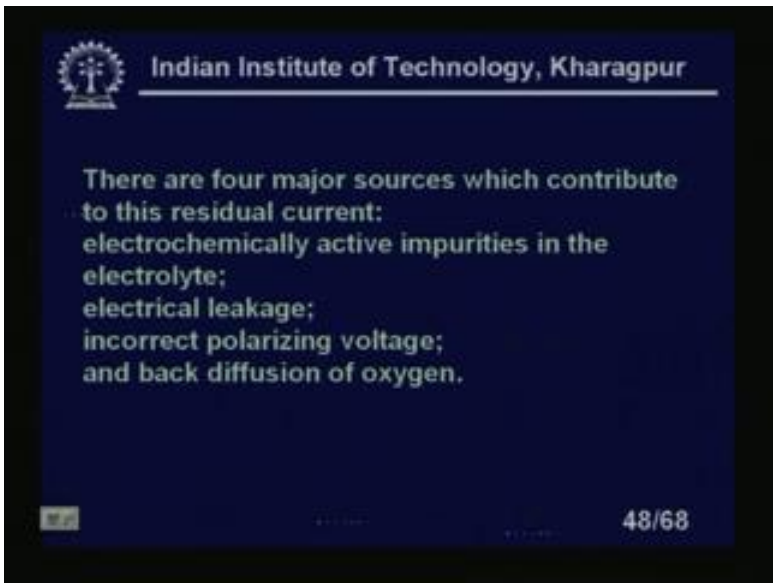

There are 4 major sources which contribute to the residual current: electrochemically active impurities in the electrolyte, electrical leakage, incorrect polarization voltage, back diffusions of oxygen.

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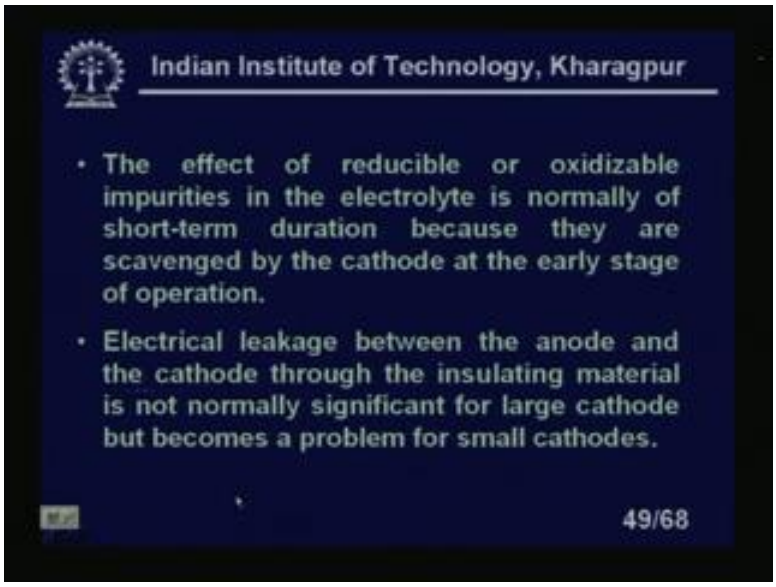

The effect of reducible or oxidizable impurities in the electrolyte is normally of short-term duration, because they are scavenged by the cathode at the early stage of operation. Electrical leakage between the anode and cathode through the insulating

material is not normally significant for leakage for large cathode, but becomes a problem for a small cathodes.

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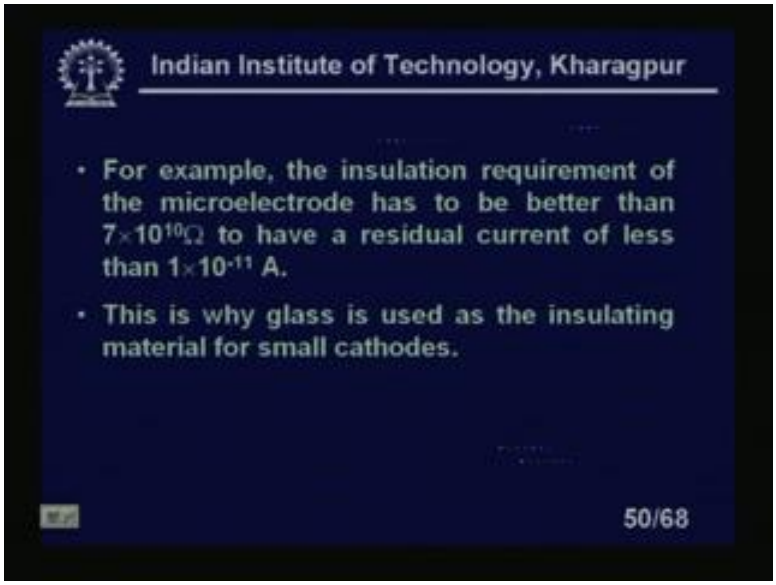

For example, the insulation requirement of a the microelectrode has to be better than ten to the power 7 into the power 10 ohm. That means, you can see it is around coming around 70 gig ohm and have a residual current of less than 10 to the power 11 ampere. That means, 0.1 picoampere. So, it is quite small this is why glass is used as the insulating material for small cathodes it will give you very less residual current.

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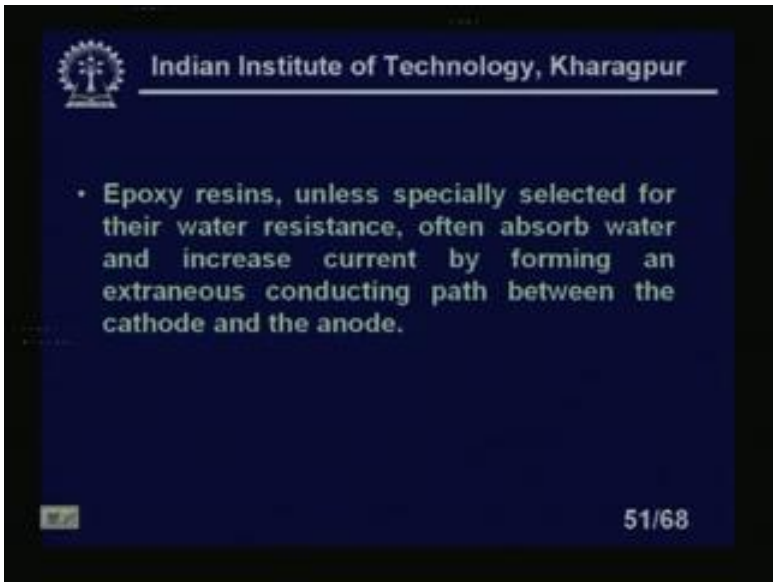

Epoxy resins, unless specially selected for their water resistance, often absorb water and increase current by forming an extraneous conducting path between the cathode and the anode. This is again problem.

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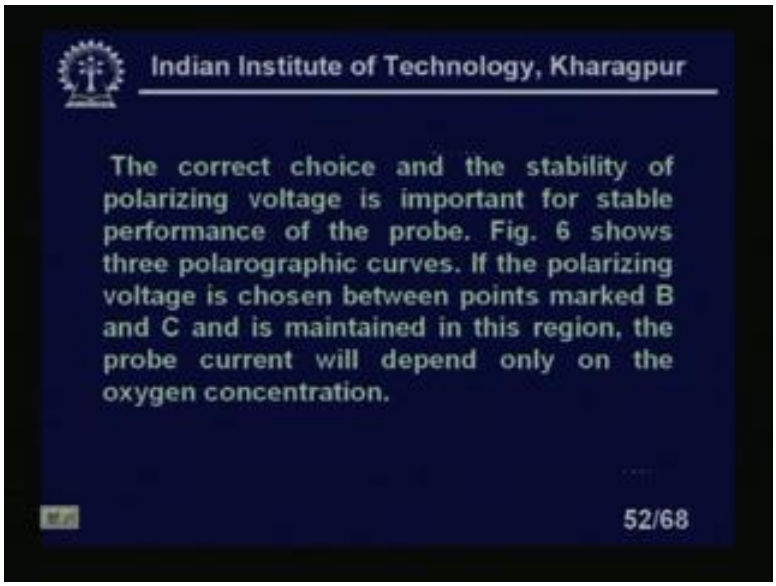

Because usually use resins to I mean to hold this different cathode anode with the systems. The correct choice and the stability of the polarizing voltage is important for stable performance of the probe. Now, figure 6 next figure shows the 3 polarographic curves which is called polarogram also. If the polarizing voltage is chosen between the points marked B and C and maintained in this region the probe current will depend only on the oxygen concentration.

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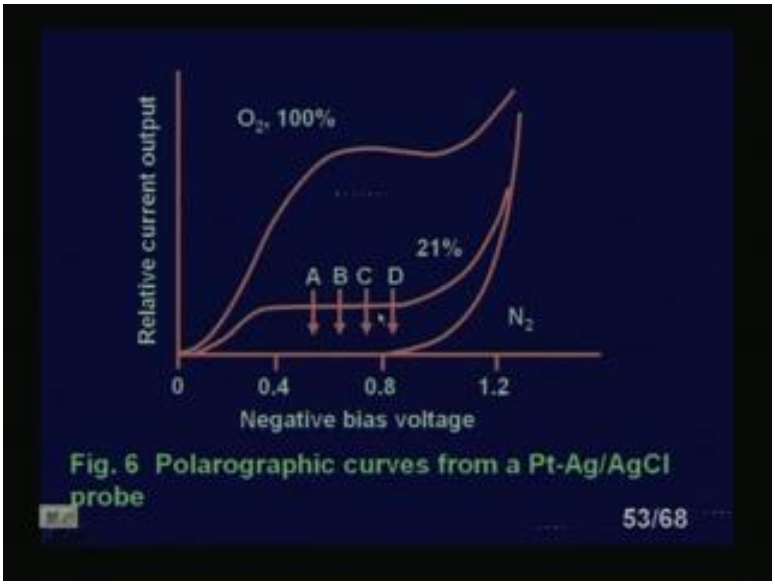

Let us look at you see here it is it is between B and C if it is if it is between B and C it is depends on the, it is B and C. So, depends on the oxygen concentrations we are talking about partial pressures of this, right.

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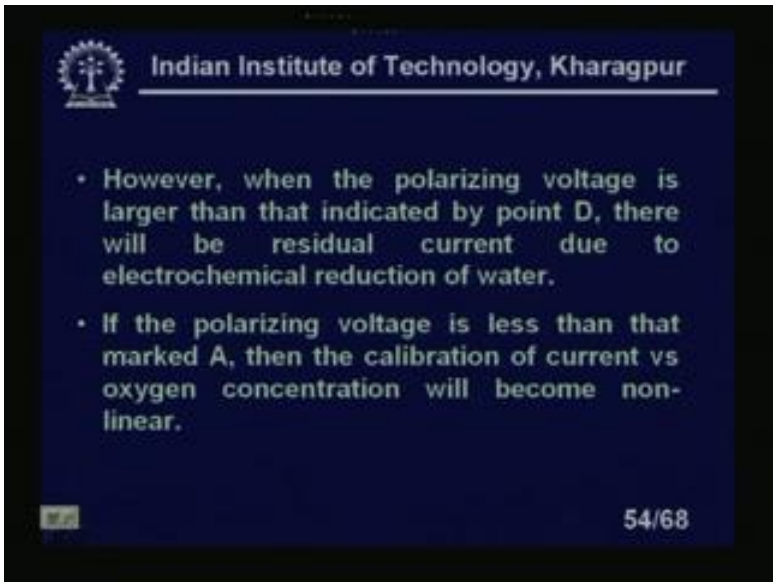

However, when the polarizing voltage is high larger than the indicated by the point D, there will be a residual current due to electrochemical gel reduction of water. If the polarizing voltage is less than that marked A then the calibration of the current versus oxygen concentration will become non-linear. Again this is non-linear region. So, if you come to the plateau region only. So, that is our desire, so that is the reason we have

marked between B and C. So, it is totally because it will depend in remain in the plateau region. So, depends only on the concentrations of the oxygen or the partial pressure of oxygen.

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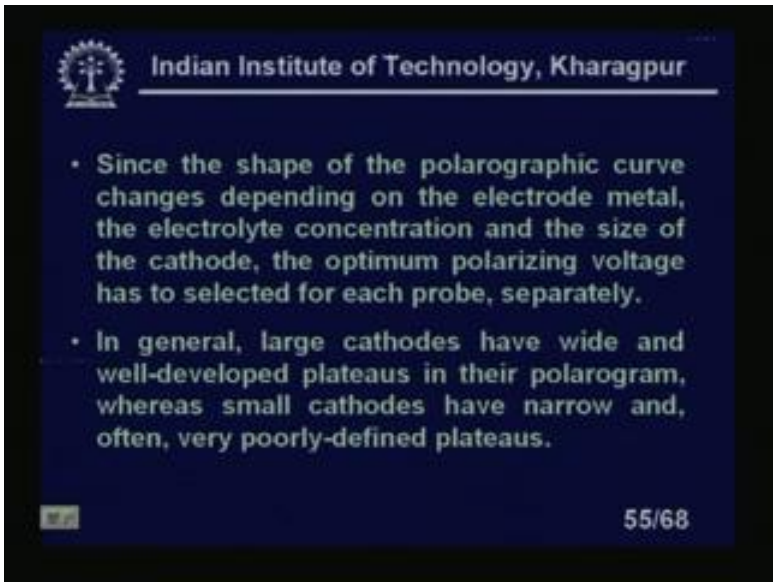

Since the shape of the polarographic curve changes depending on the electrode metal the electrolytic concentration and the size of the cathode the optimum polarizing voltage has to be selected for each probe separately. In general the large cathodes have wide and well developed plateaus in their polarogram whereas; small cathodes have narrow and often very poorly defined plateaus.

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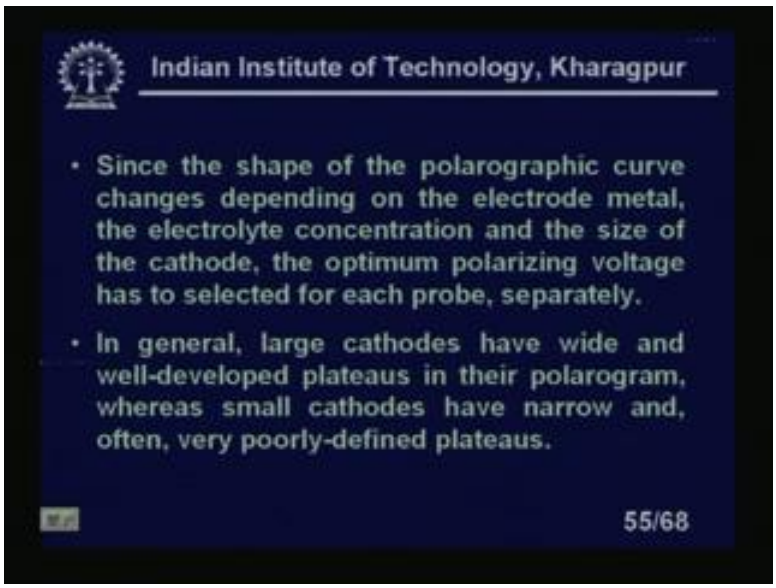

The fourth contributor to the residual current namely black diffusion of oxygen back diffusion of the oxygen from the internal electrolyte is most pronounced for the small cathodes. Mechanical designs which favor increased path length between the cathode, and the electrolyte reservoir as well decreasing the thickness of the electrolyte film between the membrane and the cathode minimize the effect.

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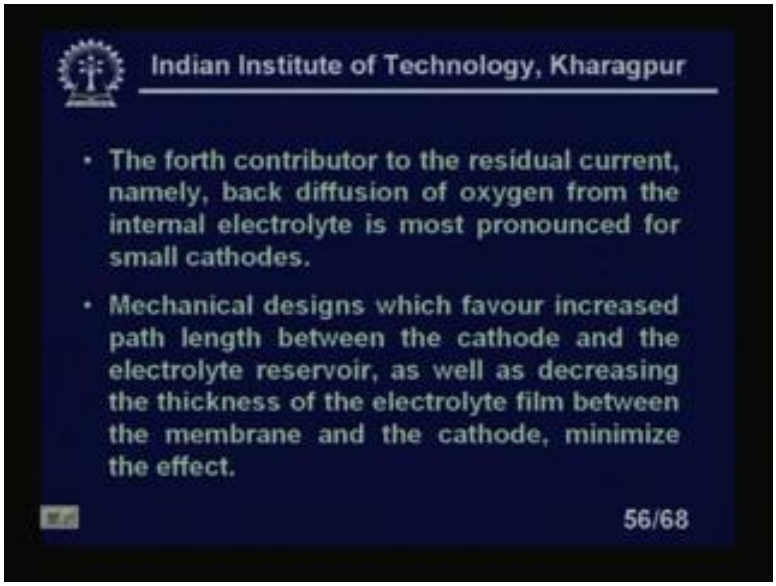

Mechanically well-designed probes with the above consideration in mind have very low residual current and are capable of measuring dissolved oxygen down to parts per billion which is called ppb instead of part per million we are calling part per billion range. Galvanic probes have been preferred in the bioreactor applications, but the disadvantage is the expendable nature of the anode, because it is bioreactor we have to make autoclaving all those thing that is the reason galvanic electrodes are most preferred. Currently available designs of the steam-sterilizable galvanic probe could be improved considerably by further decreasing the cathode area increasing the anode area and increasing the path between the electrolyte reservoirs and the cathode. This is the last one is most difficult one. A well designed polarographic probe was shown to withstand repeated steam sterilizations with a high reliability.

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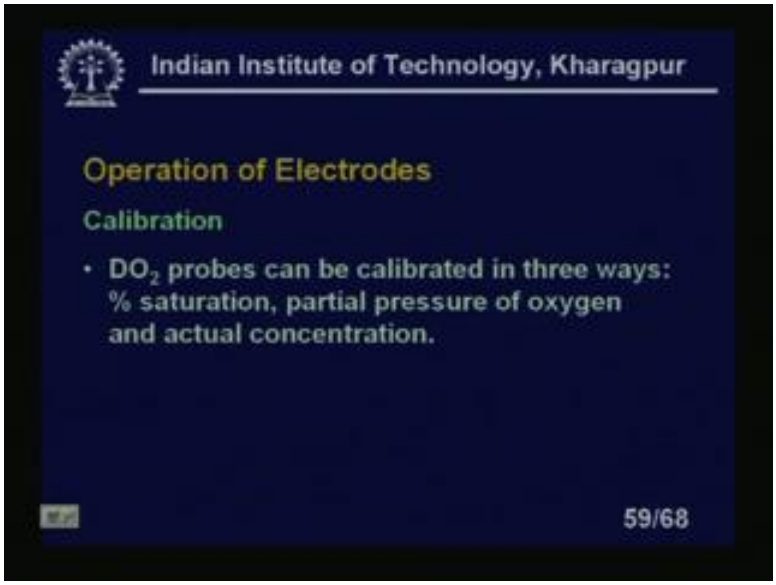

Now, operations of the electrodes, let us look at calibration this is most important thing D O 2 probes can be calibrated in three ways saturations in partial pressures of oxygen and actual concentration.

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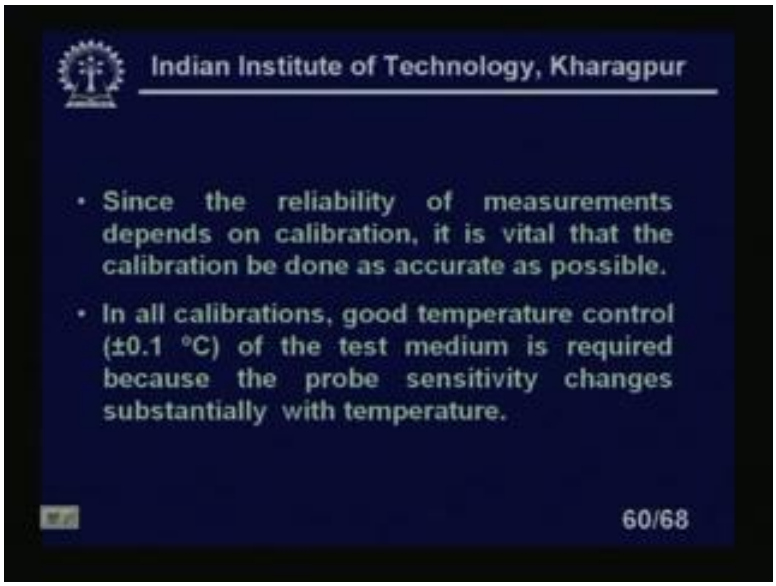

Since the reliability of measurements depends on the calibration it is vital that the calibration done as accurate as accurate as possible right. So, the calibration will show the some equation by which we can make the calibrations. In all calibrations good temperature control; that means, 0.1 degree centigrade plus minus one of the test medium is required, because the probe sensitivity changes substantially with temperature, right.

So, some sort of I mean in the, we should take care of this temperature compensation now it is in the computers we can do this I mean very nicely. So, that the output voltage which is the output which is coming out of the computer can be taken care of all this temperature compensations or I mean temperature compensation if we cannot do in the probe itself that is not a problem.

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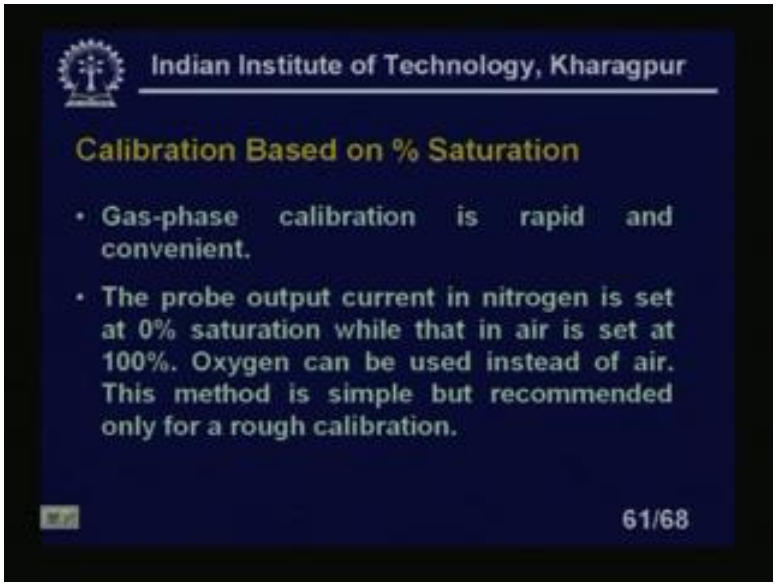

Calibration based on percentage saturation. Gas phase calibration is rapid and convenient. The probe output current in nitrogen is set at 0 percent saturation while that in the air that in the air is set at 100 percent. Oxygen can be used instead of air this method is simple, but recommended only for a rough calibrations.

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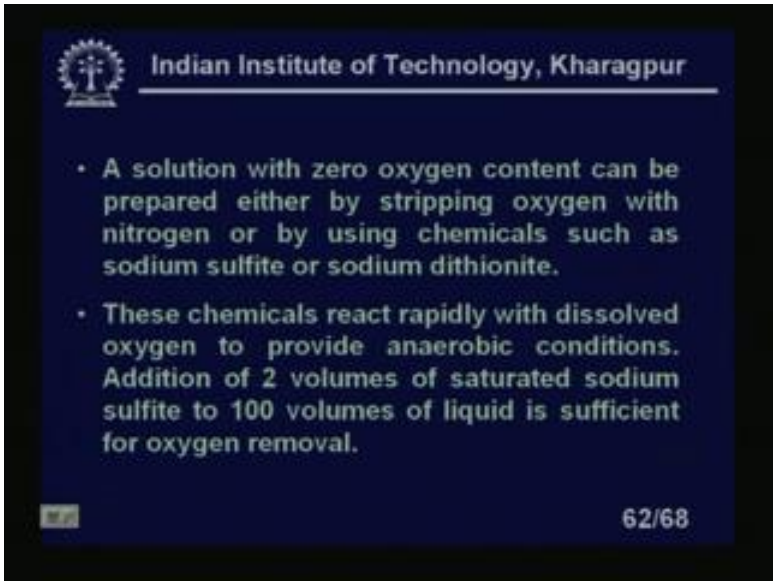

A solution with zero oxygen content can be prepared either by stripping oxygen with a nitrogen or by using chemicals such as sodium sulfite or sodium di dithionite, because by this the all oxygens will go out. These chemicals react rapidly with the dissolved oxygen to do a to provide anaerobic conditions. Additions of two volumes of saturated sodium sulfite to 100 volumes of liquid is sufficient for oxygen removal. So, that liquid now is totally oxygen free. So, I can make my calibrations that for my zero oxygen concentrations what is my output the, which is supposed to be 0 if it is not that is it is offset current or dark current.

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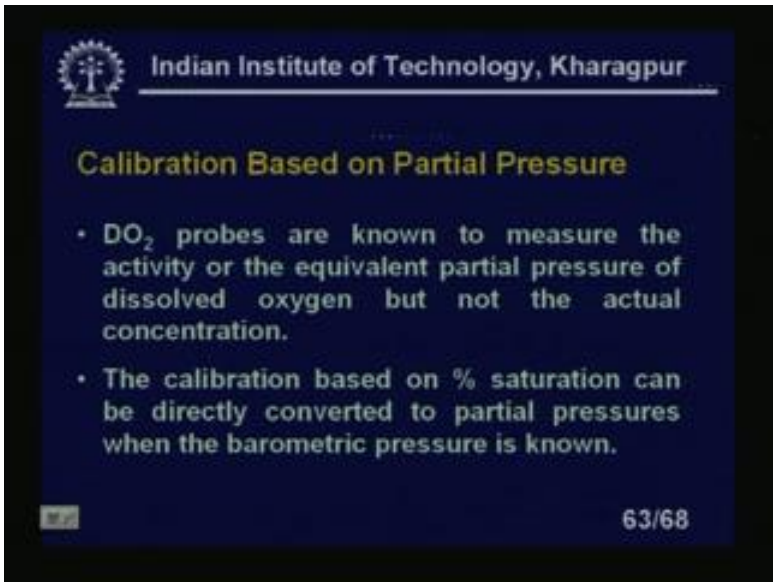

Calibration based on partial pressure D O 2 probes can known to measure the activity of the equivalent partial pressure of the dissolved oxygen, but not the actual concentrations. We actually calibrate in terms of actual concentration, but actually it is measuring the partial pressure. The calibration based on percentage saturation can be directly converted to partial pressures when the barometric pressure is known right.

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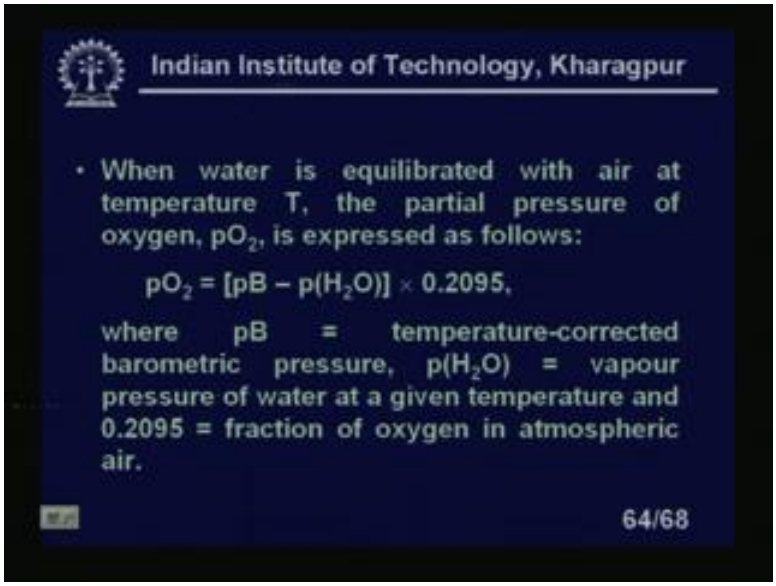

When the water is equilibrated with air at temperature T, the partial pressure of oxygen, which is written p O 2 is expressed as a following equation which is p O 2 equal to p B minus p H 2 O multiplied by constant 0.2095. What are the legends? Let us look at where p B is the temperature corrected barometric pressure p H 2 is the vapour pressure of water at a given temperature and 0.2095 is the fraction of oxygen in atmospheric air.

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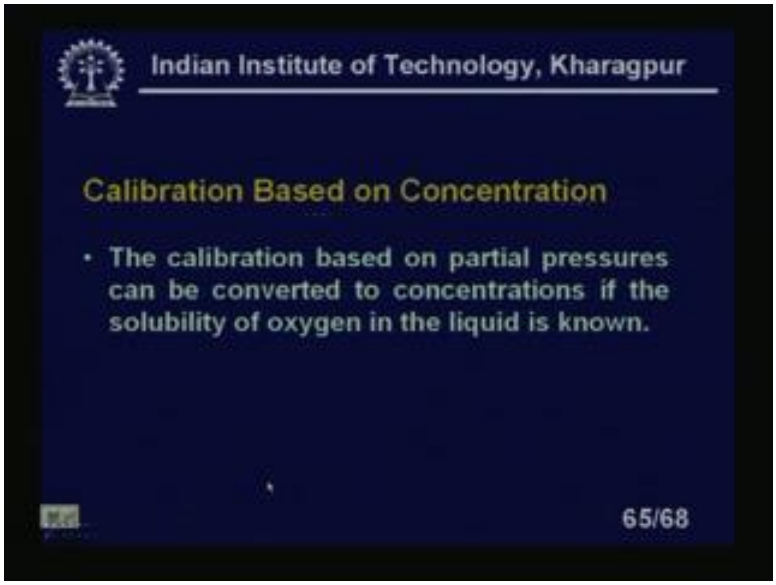

Calibration based on concentration the calibration based on partial pressures can be converted to a concentrations. As I told you if the solubility of the oxygen in the liquid is known if we know that thing how can I write.

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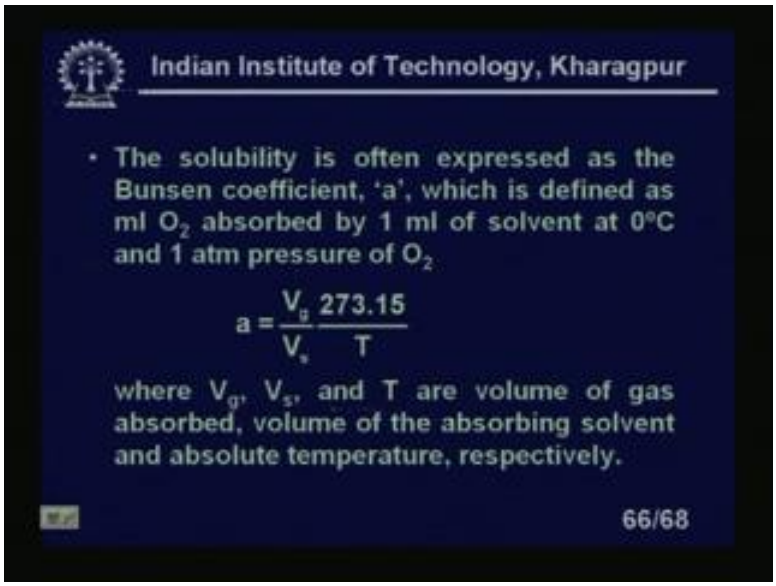

The solubility is often expressed as the Bunsen coefficient a, which is defined as the milliliter of O 2 absorbed milliliter of oxygen absorbed by 1 milliliter of solvent at 0 degree centigrade. And one atmospheric pressure of O 2 right this is my expressions a equal to Bunsen coefficient equal to V g 273.15 upon V s by T where V g V s and T are

volumes of the gas absorbed and the volume of the absorbing solvent and absolute temperature respectively.

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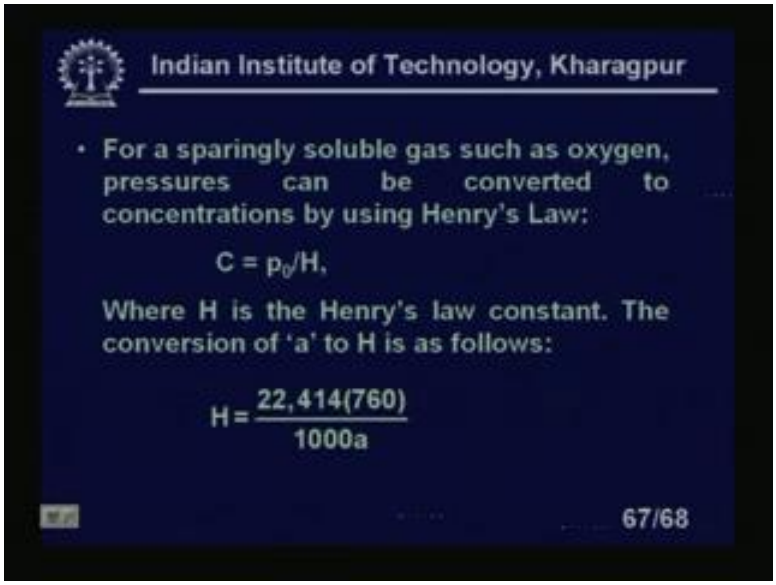

For a sparingly soluble gas such as oxygen which is very difficult to dissolve in the bulk medium a pressure can be converted to the concentrations by using Henry's law which is given by C equal to p knot by H. Where H is the Henry's laws constant and the conversions of a to H is as follows. Is H equal to 22 4.14 at 760 millimeter of H g upon 100 a plus. Please note there are some precautions we have to take. So, that I will discuss now those are like this if the probes are dead. You know that this can be rejuvenated by dissolving away the oxide layer on the anode surface with a 20 percents of C H 3 C O O H or 20 percent of H C l they are very standard; that means, if you have a I mean some sort of it is not reacting.

So, clean it at the anode surface clean the oxide layer of the anode surface should be clean with a 20 percent H C l, which is easily available in laboratory. Now, you see the electrode content in electrolyte when the chloride content electrolyte is used the chloride ion concentration will fall as it is consumed by the anode reactions and when we replace by the hydroxyl ion generated by oxygen reductions at the cathode right. Now, another important thing is you see that the current here is very, very extremely small. We have seen that this is current is coming around order of 10 to the power minus 10 10 to the power minus eleven ampere. So, almost like a I should say ten to the power I mean 0.1 picoampere which is extremely small this type of small current right. Now, so special

amplifier is required this amplifier will not do alone, because there is it will introduce a lot of noise.

So, the common mode noise I mean we have to use some differential technique by which we can I mean eliminate this type of problem. Because amount of current there is some inherent noise in the systems you will find thermal noise. Because, so that type of things because when you will transmit the signal over the even the probe length whatever the small it when it is going to the meter itself we will find it has some length. However, small it may be, because you cannot immediately, you cannot connect a transmitter just over a probe itself a certain amount of length is to be I mean you have to certain amount of layer length of the wire is to be connected.

So, that wire also will give some noise. So, that type of things can be eliminated if you use a instrumentation amplifier and the input of this current transmitter. So, that the common mode noise will go away, so the only differential mode signal will be amplified. So, this is to be I mean we have to keep in mind. So, this I mean these are the most important thing we should think while using the D O 2 sensors. But the some precautions you have to sense depending on the what are the requirements accordingly we will choose on the pressure will come P knot equal to A b 1 by A b 2 I 1 by I 2 P 1 minus P 2 right. So, this actually will give you the direct this you see the output pressure is again the function of P 1 minus P 2 which is actually calibrated in terms of the flow. So, with this I come to the end of the flapper nozzle system.