Electrochemical Technology in Pollution Control

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Greetings to you. We have been discussing about the Sensors and the sensor world. I had told you in my last class that the physical size geometry selection of various components and all those construction etcetera, usually depend on the intended use. They can be very small miniaturized micronized or they can be in centimeters where they can be of various sizes. Quite often, the final design is results in a compromise between various performance parameters in the Electrochemical Sensor.

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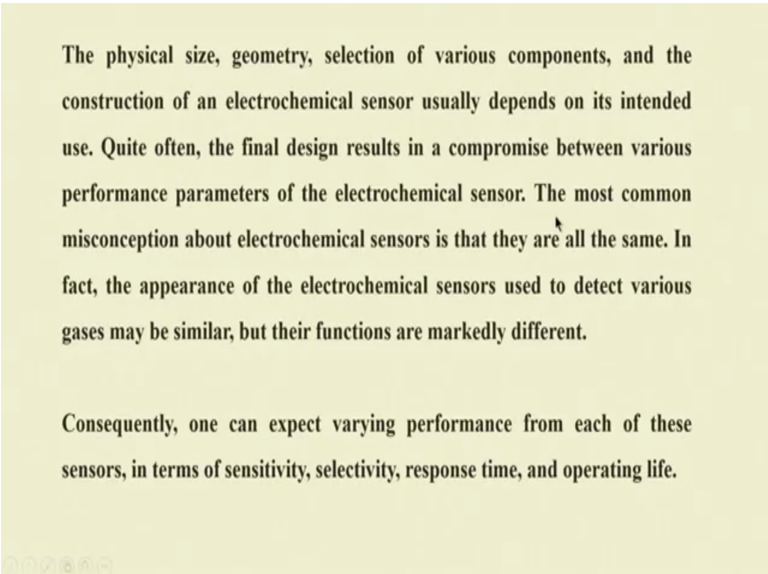

The most common misconception about electrochemical sensor is that they are all the same. Actually, this is a very common mistake lot of people use, I have come across people. Even in Indian Institute of Science where people say they had developed a sensor they wanted me to check the sensors for various things.

Some one day one of my colleague came to me and told me Doctor Mudakavi I have developed a sensor for carbon monoxide, can you check and tell me how long it will be useful how much useful it will be. Then I told him how did you make the sensor? Then he said I took this compound that compound made an electric membrane, put it in two connector etcetera something like a MOSFET and then I have made the sensor.

Then I said how do you know that your sensor works for carbon monoxide? Then he said oh it is very simple all sensors are same you know. I have made so many electrodes, so many sensors, all of them show a deflection whenever there is carbon monoxide. Then I asked how do you generate carbon monoxide? Then he said no, that is very simple I say. I just take a piece of paper burn it and then that gives carbon monoxide it gives me a signal.

So, all I want you to do is do not worry about such things, but I want you to test for your for my this thing quantitative aspects. Then I said look here sir, the problem is you think that you are all sensors are same. Unfortunately, they are not. The problem is the whenever you burn a paper it contains 400 organic compounds, are you aware? Then, he said no, no nothing, I am not aware I thought everything is burnt into carbon monoxide and carbon dioxide.

Then I told him that [FL] it is not that way the there are 400 organic compounds, when you burn paper all of them are in the air. So, how do you know that your only your carbon monoxide is reacting to your sensor and others are not? Then he then he was quiet he did not know what to say. So, then I asked him one more question carbon monoxide is being produced definitely when you burn paper there will be oxygen also, carbon dioxide also will be produced.

So, which one is the sensor works, for carbon monoxide or carbon dioxide? I will assume that all other compounds are very less or minor in quantity. He was flabbergasted; he did not know what to say then he said then how do you want to test? Then I said you bring your sensor we will take carbon monoxide and set up a system of your sensor fit it into a p H electrode or some other electrode where I can measure the potential.

And, then we will pass the carbon monoxide in different quantities not 100 percent; because the sensor should work in 10 raise to minus 6 molar concentrations. So, we will we will devise a system for dilution of carbon monoxide into 10 raise to minus 6 molar; then we will pass that gas and then if it shows a deflection I will be ready to work for you. It never proceeded further from that point onwards.

So, the coming back to this, the most common misconception people think is in all electrochemical sensors are all the same that is wrong. So, in fact, the appearance of chemical say electrochemical sensors used to detect various gases may be similar. See all they will show is a something like a button like this and then this button will have some perforation or something like that behind that is the sensor. So, all may look the same, but their functions are different, responses are different and then inputs are different. So, how do you say that such sensors are all same? It does not make sense.

So, the there is lot of things to learn for us how to make sensors if you are working in a sensor, but more than anything, a sensor should be defined in terms of the interferences it can tolerate or the conditions in which it can operate or non-operate not operate. So, if we can measure do that that would be a wonderful contribution to the science and technology of the sensors. Nowadays I do not find such papers, which even describe the interference of the chemicals to these sensors electrochemical sensors.

So, if we have to do that, if the functions are different one can expect varying performance for each of the sensors also. So, what would be the parameters of performance of a sensor? First of all, I would say that it is the sensitivity at what is the lowest detection limit of the sensor for the desired component? That is number 1; and selectivity - if there are other compounds are they responsive to the same sensor and if they are responsive up to what level they are responsive? Is it same as the sensor in which for which it is made or is it very 100 percent lower, 100 percent higher or same, equal etcetera. So, the emf you see finally, it is the emf that we measure basically. So, whatever is the chemistry of the sensor the measurement is always emf.

So, if there is any interference from any chemical it will not show me as interference, but it will show some current reading. It is for the chemist to interpret what is the actual response of the analyte and the other concomitants. So, we sensitivity is important; selectivity is important and response time is important how much time it takes to show there is set up the equilibrium and how long it will operate, that is also important that is shelf life.

The shelf life of a sensor is a funny thing. If you buy a sensor today, the sensor machine works, but the sensor will go off after two years it would not be operatable at all. Whether you use it or not the sensor will not be operating. So, what to do? So, such problems are very common among the sensors. And especially the maintenance people if they are engineers they are simply not made aware of such things they will say oh we have put up the sensor there it will it is there working sir. So, it will be showing some reading, but who is there to check whether the accuracy of the sensor or is the serving the intended purpose of the sensor that is very important.

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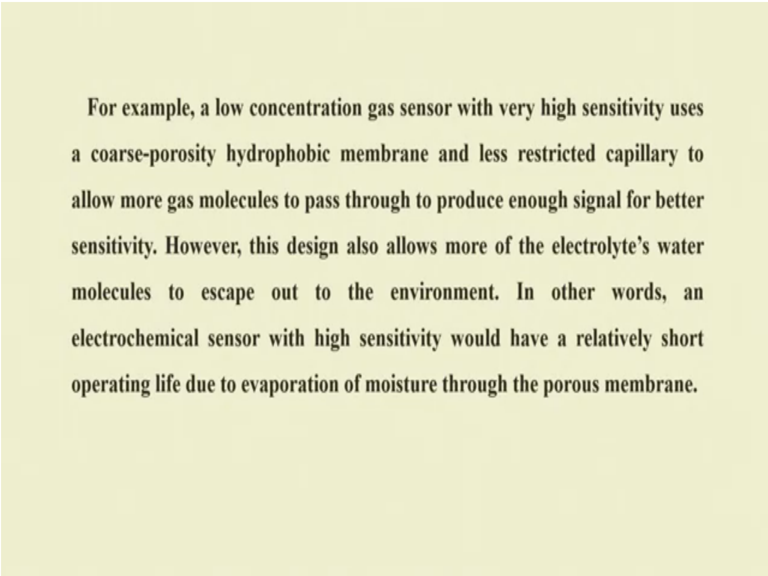

So, here I can tell you that for example, a low concentration gas sensor is there with very high sensitivity what does it do? It uses a coarse porosity hydrophobic membrane. So, basically it has a coarse porosity hydrophobic membrane coarse porosity why coarse porosity? Because we want the whenever the sensor is there we want the sample to reach the sensor, but sensor should not be open to environment. So, I need a filter. So, this filter should be able to remove all the particulates dust, water, vapor and other non concomitant other gases which are present in the sample system.

So, I need a coarse porosity hydrophobic membrane and less restricted capillary smaller capillary to allow more gas molecules to pass through to produce enough signal for better sensitivity. So, these are the kind of requirements whenever you make a gadget for electrochemical sensors. So, such a design also allows more of electrolytes water molecules to escape out into the environment. In other words, an electrochemical sensor with high sensitivity would have a relatively short operating life due to the evaporation of moisture through the porous membrane.

So, what do we want to do? We want the water molecules if the electro membrane should be in contact with vapour. So, it must have a chamber where the water molecules are always there. So, even if it escapes more water molecules should be there and the humidity should be maintained properly. So, if the humidity is not maintained again the equilibrium will be disturbed. So, the relatively operating life of a sensor is always due to evaporation of the moisture through the porous membrane which can lead to erroneous results.

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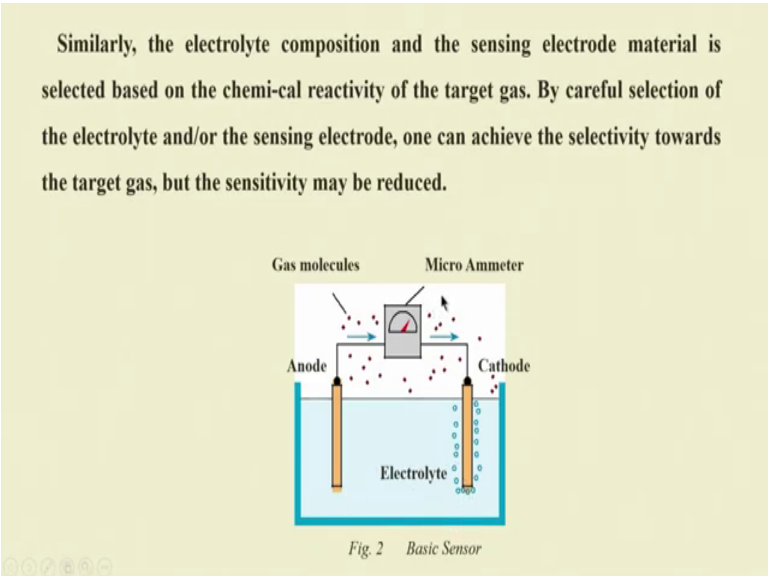

Similarly, the electrolyte composition and the sensing electrode material is basically selected on the chemical reactivity of the target gas. By careful selection of the electrolyte and sensing electrolyte, we can achieve the selectivity towards the targeting gas and the sensitivity, but the sensitivity may be reduced. The more selective the sensitivity will be less; if the selectivity is high sensitivity will be more. So, the both of them are inversely related to each other.

So, here we have a basic sensor design. I have two electrodes – one is anode and another is cathode. And here I have an electrolyte here there is a cyst there is a closed compartment containing enough water vapors ok, here I am showing them by dots. So, there will be current will be flowing from the anode into cathode and like that and ions will be passing through like this. Cations towards cathode anions towards anode and all other things remain the same ok.

Here I have the gas molecules and here is a micrometer to measure the current and the electrolyte and basic design is same. So, such would be a gas membrane and the gas is supposed to diffuse through and then react at the electrode surfaces.

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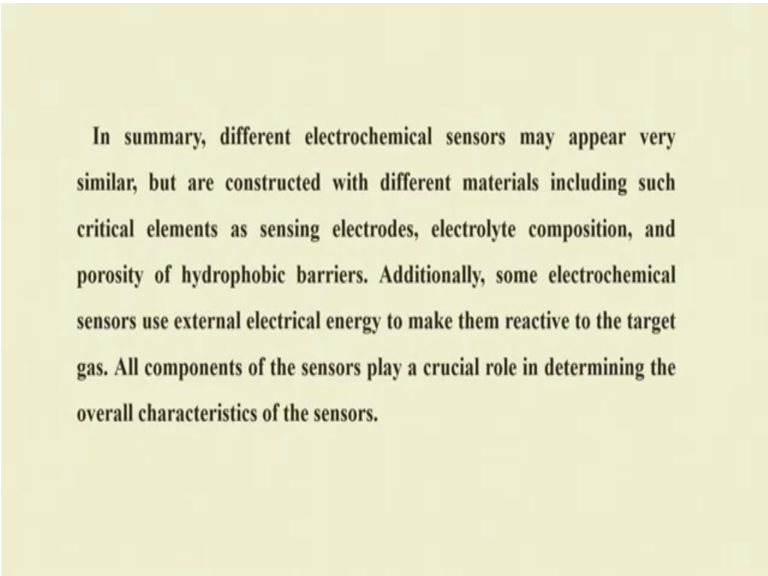

So, in summary, different electrochemical sensors may appear very similar, but they are constructed with different materials that include critical element as sensing electrode, electrolyte composition, porosity of the hydrophobic barriers etcetera.

So, additionally some electrochemical sensors use external electrical energy also we need. So, there is a need for incorporating a battery or a capacitor into the electrical circuit to make them reactive to the target gas. Then all components of the sensors therefore, they play a very crucial role in determining the overall characteristics of the sensors.

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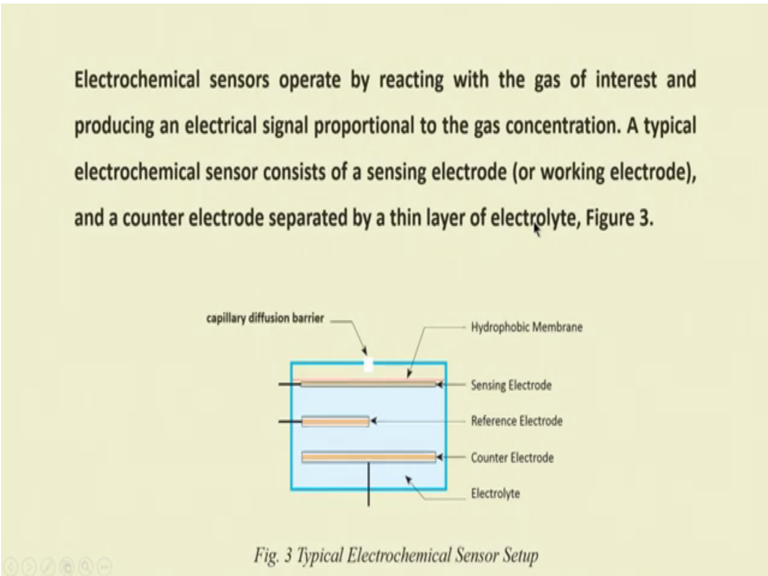

Electrochemical sensors basically operate by reacting with the gas of the interest and they produce an electrical signal proportional to the gas kernel. This is basic theory. There is nothing very new about this sentence. A typical electrochemical sensor consists of a sensing electrolyte sensing electrode, it is not the electrolyte, it is the electrode or working electrode and a counter electrode separated by thin layer of electrolyte.

So, again I am going back to the previous slide, this slide. So, I need a sensor here somewhere in between and this sensor is designed like this. I have an electrolyte here and one connector is here, another connector is here. And, here I have a reference electrode and sensing electrode. This is our sensor and this is the counter electrode, and electrolyte here is a hydrophobic membrane. And, here I have a small capillary for diffusing the gas molecules through the say hydrophobic membrane and on to the sensing electrode. So, that is how we make their design.

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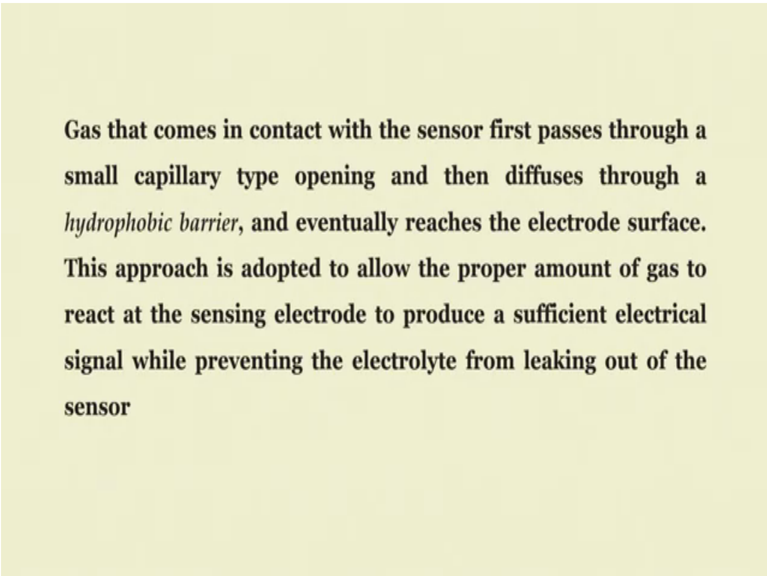

So, gas that comes into contact with the sensor must first pass through a small capillary type opening and then it must diffuse through a hydrophobic barrier; this is all simply explaining the same thing what I have shown here. I have put it in record so that you can go through that at your free time. So, it must pass through the capillary opening and diffuse through a hydrophobic barrier and eventually it must reach the electrode surface.

This approach is adopted to allow proper amount of gas to react at the sensing electrode to produce a sufficient electrical signal while preventing the electrolyte from leaking out of the sensor. This is also very important. So, here the electrolyte should not be leaking out from inside the sensor material. So, that means, it must remain in working condition as long as possible and then only it will work. So, the inner solution in the inner circuit inner part of the electrode should not leak out.

Then what we need? We need the sensing electrode, must have electrical connection for taking out the current a emf for measuring the emf and then sufficient electrical signal should be there for us to record. And, once you record there is no other barrier except that you can include all the niceties like display and then display in voltage, display in current, display in the concentration itself directly; so that the person who is handling need not be trained in the chemistry aspect, but in handling the data. Data analytics is a big field nowadays and that can be organized, but the basic requirement of chemistry must be met if you want to conduct the electrochemical sensor to work under difficult conditions.

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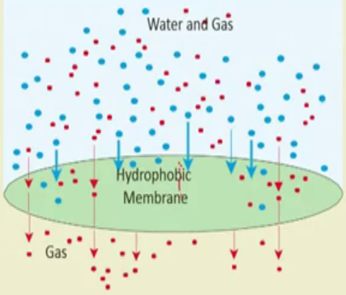

Fig. 4 Hydrophobic Membrane: prevents liquid electrolyte from leaking out

So, this is a modified picture of the sensor the hydrophobic membrane is a imagine like this is a cylindrical electrode system and this is the water and gas molecules above this I have the gas molecules coming through the membrane. So, this is the type of mechanism. Lot of work has been done regarding the transport properties of the gas, water and through the quality preparation of the membrane, particle size and pore size. And all those data I will not go into details because that itself will be a big topic for some other course, not for this course. The aim of our course is slightly different. We have to think about the pollution aspects also.

And, electro chemical sensors play a very important role in sensing the quality of a effluent whether it is gas or liquid continuously online monitoring. Nowadays since last year there is a rule was imposed on many of the industries to put on online continuous sensors to sense p H, dissolved oxygen, COD, BOD and many other parameters and transmitted to the central pollution control board online throughout the year 24 bar 7.

So, in such cases sensors become very important in most of the industrial applications and that has got a lot of things to do with our course.

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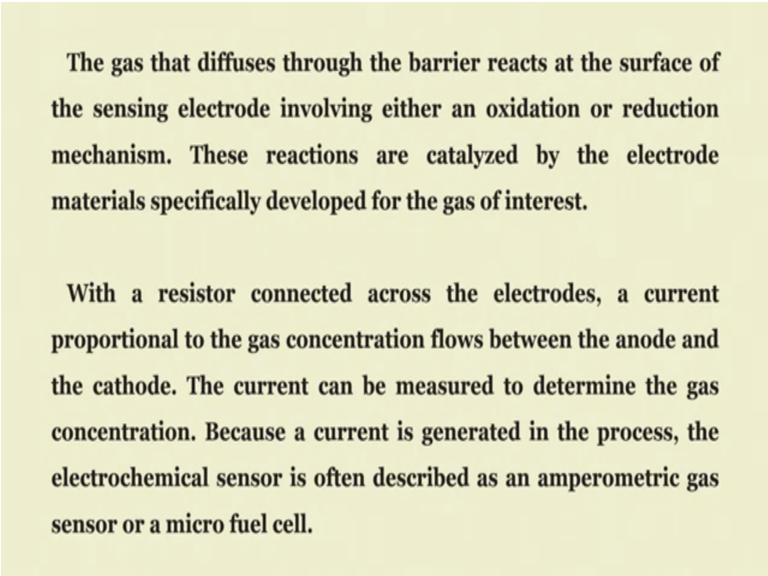

So, the gas that diffuses through the barrier reacts at the surface of the sensing electrode involving either an oxidation or reduction mechanism. We are not going into details of these because we have discussed all these earlier. And these reactions are catalyzed by the electrode materials specifically developed for the gas of interest. In petrochemicals for example, people want to know what is the ethylene gas they want an ethylene gas sensor and then they need the gas for gas sensor for propylene and hydrocarbons and then methane, VOCs and so many other gases.

And, in several industries several types of electrochemical sensors are needed. So, what we need to do? We need a resistor connected across the electrodes and a current proportional to the gas concentration that is important. That flows between the anode and cathode and the current can be measured to determine the gas concentration. Because a current is generated in the process, the electrochemical sensor is of10 described as amperometric gas sensor or a micro fuel cell. So, micro fuel cell also does the same job and then the current is measured.

And, even Karl Fischer titration is also some sort of amperometric process only; because we are measuring the current that is being removed because the iodide ion reacts with the pyridine and SO 2 and methane methanol to remove the iodine ions and then current approaches 0 that is the electrochemical end point. We can even use the Gran plots for that.

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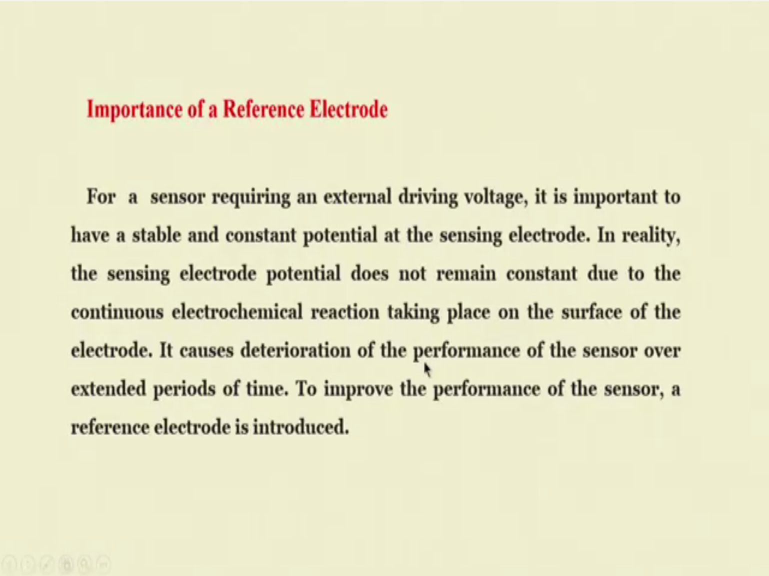

So, what is the importance of a reference electrode? So, for a sensor requiring the an external driving voltage, it is important for us to have a stable and constant potential at the sensing electrode. This is very important especially, because the sensor that requires external driving force the voltage fluctuation can cause lot of trouble in the a potential measurement.

In reality, the sensing electrode does not remain constant due to continuous electrochemical reaction takes place, there will be voltage fluctuation, there will be many other ah stoppage of voltage for some reason or the other and all these things play havoc on the say a sensing electrode potential. So, it causes deterioration of the performance of the sensor and oh if it continues for longer time, it can extend over a long period and then it may start malfunctioning also.

Therefore, to improve the performance of the sensor, a reference electrode is definitely introduced.

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This reference electrode is placed within the electrolyte in close proximity to the sensing electrode. A fixed stable constant potential is applied to the sens- ing electrode. The reference electrode maintains the value of this fixed voltage at the sensing electrode. No current flows to or from the reference electrode. The gas molecules react at the sensing electrode and the current flow between the sensing and the counter electrode is measured and is typically related directly to the gas concentration. The value of the voltage applied to the sensing electrode makes the sensor specific to the target gas.

So, this reference electrode is placed between the electrolyte in close proximity to the sensing electrode. So, a fixed stable constant potential is applied to the sensing electrode all in all. The reference electrode maintains the value of this fixed voltage at the sensing electrode. Its function is to maintain the correct value of the potential at the sensing electrode so, no current flows to or from the reference electrode. So, it has no other basic function.

The reference electrode has no other basic function except to provide the required potential to the gas sensor. So, the there is no current. The gas molecules, what do they do then? If there is only when there is exact quantity of the potential at the gas sensing electrode, the gas molecules will react at the sensing electrode and the current flows between the sensing electrode and the counter electrode it is not the reference electrode.

So, if you remember the previous picture, you should see that this is the reference electrode. This job of this reference electrode is only with these two with this electrode and it gives a constant potential. So, gas molecules react at the sensing electrode the value of the voltage applied to the sensing electrode makes the sensor specific to the target gas. This has something to do with the target gas; because it has to be standardized with respect to the particular gas before being put in an operating field.

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The micro fuel cell type electrochemical sensors do not require an external driving voltage. For example, an elec trochemical sensor specific to oxygen has an anode, either Pb or Cd, that supplies electrons for the reduction of oxygen at the cathode. During the oxidation of the anode, the electrons are released which then travel via an external circuit to the cathode where oxygen molecules consume the electrons as follows:

So, the microcell fuel cell type electrochemical sensor do they do not require an extra driving force, they do not need extra driving voltage. For example, you can take electrochemical sensor specific to oxygen; it has an anode, it has a anode made of lead or cadmium that supplies electrons for the reduction of oxygen at the cathode. So, it is already there.

So, during the oxidation of the anode, electrons are automatically released which then travel via an external circuit to the cathode where oxygen molecules consume the electrons. So, the reaction is very simple and there is abundance of electrons in the sensing electrode containing cadmium or lead. So, that itself acts as a driving force for the electrochemical sensor.

So, what are the types of reactions that happen at the electrode, if I use lead as a sensing electrode lead as a cathode?

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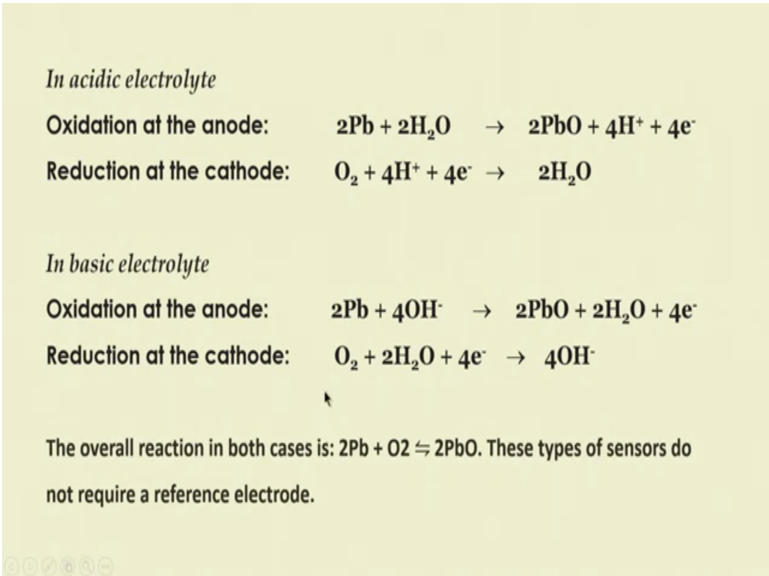

So, look at the slide now. In acidic electrolyte, I have oxidation at the anode and then I have lead, what is the reaction? 2 P b plus 2 H 2 O going to 2 P b O, lead oxide and then, 4 H plus 4 e; so, acid is being generated here H plus. So, this reaction happens at the anode; for this reaction to proceed also, we need voltage high voltage. And, then as usual reduction happens at the cathode. So, the oxygen gas is reduced to using these 4 hydrogen ions and 4 electrons to 2 H 2 O addition of hydrogen is reduction. So, you can try to remember that.

So, this happens in acidic medium, but what happens if it is in alkaline medium? There also same similar reaction takes place, but at different voltage and the reaction can be written as 2 P b plus 4 O H minus goes to 2 P b O plus 2 H 2 O releasing 4 electrons; this is a separate reaction but, the reaction medium here is alkaline. Here it is water, slightly acidic medium and here it is alkaline medium. And, the oxygen molecules can also pick up these 4 electrons and water; water is always there whether it is alkali or acid and ah they will pick up and forming 4 OH minus ions. So, this is the oxidation.

So, the overall reaction what is the reaction? You can add the anode and cathode reactions and then subtract or remove whatever is common. For example, if I add these two and these two, there will be OH on the left side OH 4 OH on the left side so, these two this will cancel. It is just like algebraic equation 4 x here, 4 x here also why written 4 x remove 4 OH minus and then there is 2 H 2 O here, 2 H 2 O here that can be removed and what remains is 2Pb plus O 2 going to 2 P b O, this is a reversible reaction.

So, these type of sensors do not require a reference electrode at all. Why? Because whether it is oxidation or reduction the products remain the same.

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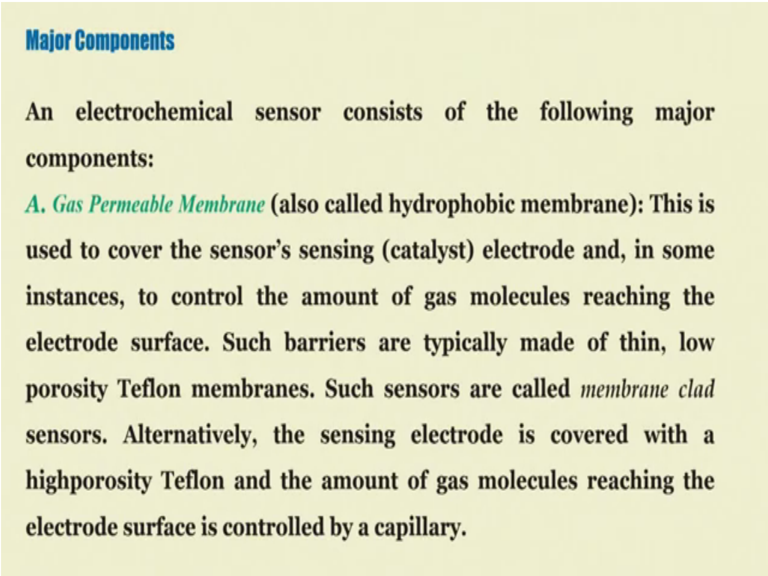

So, what do what does a an electrochemical sensor machine will consist of equipment, an electrochemical sensor what does it consist of? You can you can make a guess, it is very simple. First is a gas permeable membrane also called as hydrophobic membrane. This is used to cover the sensors electrode that is sensing electrode that is catalyst containing lead, in some instances to control the amount of gas molecules reaching the electrode surface. So, the porosity is important.

And, then such barriers are typically made of thin low porosity Teflon membranes, such sensors are called membrane clad sensors. You should remember this, such barriers made of thin low porosity Teflon membranes covering the whole sensor is known as membrane clad sensors. Alternately I can say a sensing electrode is covered with a high porosity Teflon also.

And, the amount of gas molecule reaching the electrode is controlled by a capillary; that means, the sensing electric gas can pass through the high porosity membrane and reach the reach the sensor or let everything pass and allow a capillary to take the gas molecules until the point of sensor is reached.

So, two ways of controlling and depending upon the detection sensitivity and selectivity what you need in a for a given sensor? So, you can take a capillary, you can take a small tube or you can take the whole surface area, either way it depends upon the response what you are measuring and the capability of measurement. So, such sensors containing capillary are called as capillary type sensors.

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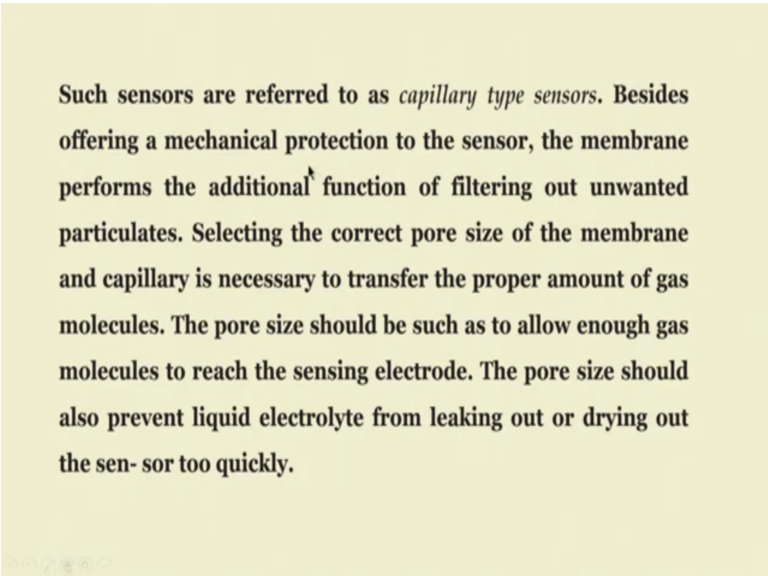

So, the besides offering a mechanical protection to the sensor what do they do? The membrane performs the additional function of filtering out the unwanted particulates. This is very important. I have been telling you that, the particulates in the air or in the sample gas will adversely affect the sensor material.

So, if the sensor material member if it is a small membrane with a porous this thing it is supposed to allow gases to pass through, but not the particles. Particles may pass through if they are very small come or comparable to the gas, but not if they are thick. If the particles are thicker they will go and stuck get stuck on the membrane and may not allow the gas to pass through. So, after some time the membrane gets clogged and you would not get any result.

So, selecting the correct pore size of the membrane and capillary also is very essential and important to transfer proper amount of gas and you can call it gas or gas molecules gas is better, I do not like gas molecules. So, the total quantity of the gas should be designed in such a way that the sensor gives you an appropriate voltage which can be measured using the given electrical circuitry.

So, the pore size should be such as to allow enough gas to reach the sensing electrode. So, it may be continuous or it may be in puffs, depending upon. If it is a diffusion controlled system then puffs continuous sensing makes more sense. The pore size should also prevent liquid electrolyte from leaking out. So, the liquid should not come out so, the pore size should be very very small.

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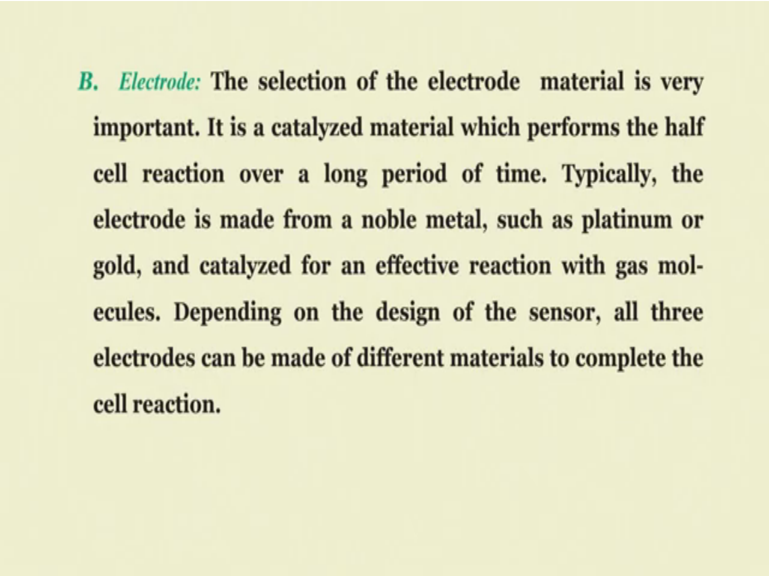

Now, we talk about the electrode. In the electrode what do we have? The selection of the electrode material is very important, it is catalyzed material which performs the half cell reaction over a long period of life that is a metal as we have already discussed lead or cadmium, which can give electrons for long time is more than sufficient for a such a system and typically the electrode should be made from a noble metal. Why? Noble metals are inert to alkali inert to acids inert to other chemicals etcetera.

So, noble metals are always preferred in such a sensor materials and that is why platinum, gold, silver, palladium such materials are noble materials. Of course, use of gold etcetera becomes a little tricky because if we make lot of sensors there will be enough gold for recovery.

But, catalyzed the reaction will be very fast in presence of platinum or gold, but palladium if you use there will be chances of poisoning. In copper also is a fine a very fine system, but very prone to interaction from acids, alkalis etcetera it may rust there may be copper sulfate deposit and many other things are possible. So, for such reasons we use noble metals preferably silver; silver also rarely we use, but gold, platinum and palladium to some extent they are all useful for gas sensors.

So, depending on the design of the sensor, all three electrodes can be made of different materials to complete the cell reaction.

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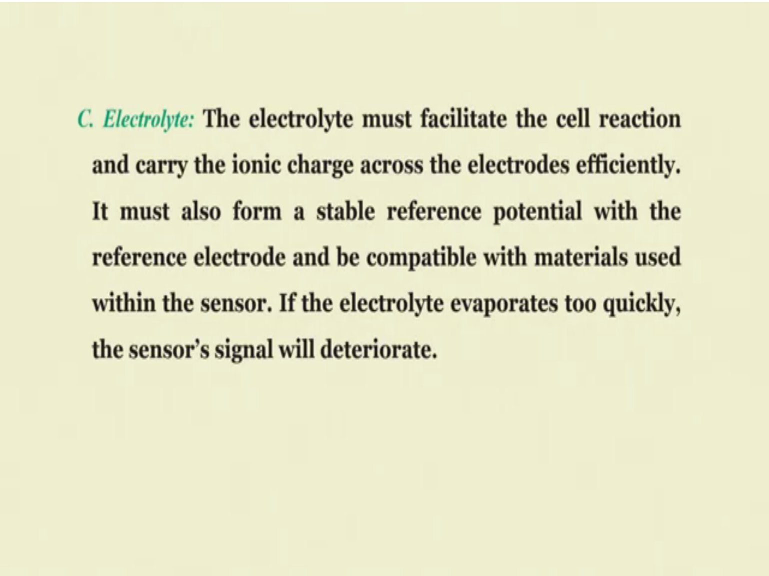

So, then we talk of the electrolyte. So, what type of electrolyte should be there? That can facilitate the cell reaction and carry out ionic charge across the electrode efficiently. That means, it must be some sort of aqueous solution the only in most of the time aqueous solutions carry the ions very efficiently. Sometimes there may be a mixture of methanol acetone or couple of organic solvents can be used as a mixers, but the aqueous solution is more than enough.

So, there it must form a stable reference potential with the reference electrode and be compatible with all the materials used within the sensor and if the electrode lyte evaporates too quickly then the sensor signal will deteriorate. Therefore, we try to increase signal we try to if the electrolyte evaporates too quickly the sensor signal will deteriorate. So, you must keep on topping it up basically that is what I was trying to say. We increase the topping up percentage with the electrolyte or with the water depends upon how much electrolyte you are losing.

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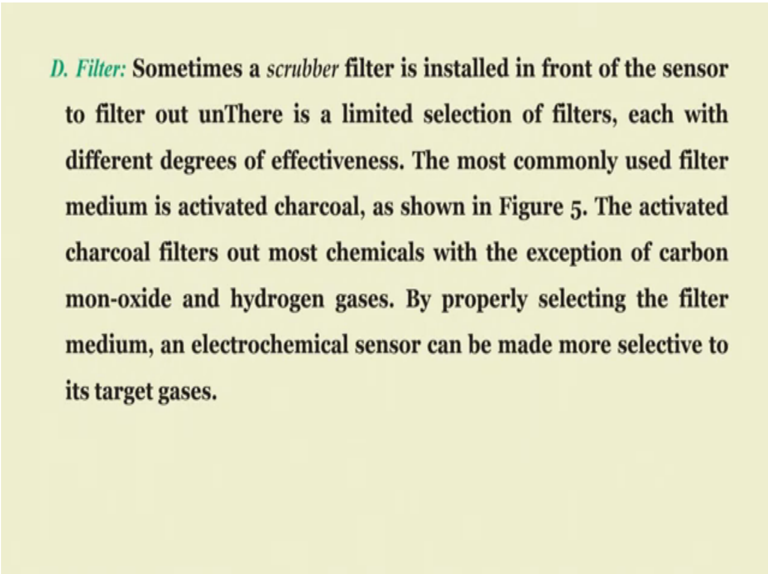

Then we also discuss a little bit about the filter; because filter as I have told you it is installed in front of the sensor to filter out coarse particles the. So, there is a limited selection of such filters each with different degrees of effectiveness because it is the first filter on their way to sensor.

So, the most commonly used filter is activated charcoal. So, that is shown there. The activated charcoal filters out most of the chemicals with the exception of carbon monoxide and hydrogen gases. So, if you want a determination of carbon monoxide and hydrogen, you must use activated charcoal filter. So, they will pass through. So, by properly selecting the filter medium an electrochemical sensor can be made more selective to its target gas.

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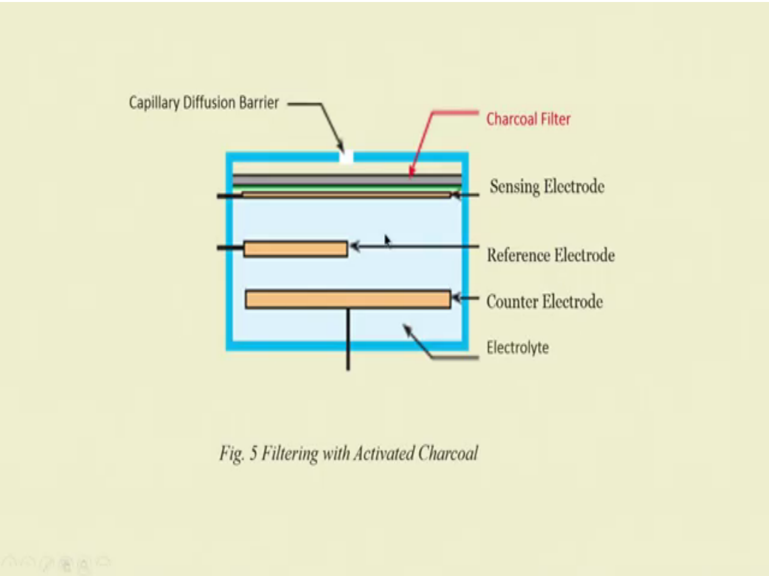

Fig. 5 Filtering with Activated Charcoal

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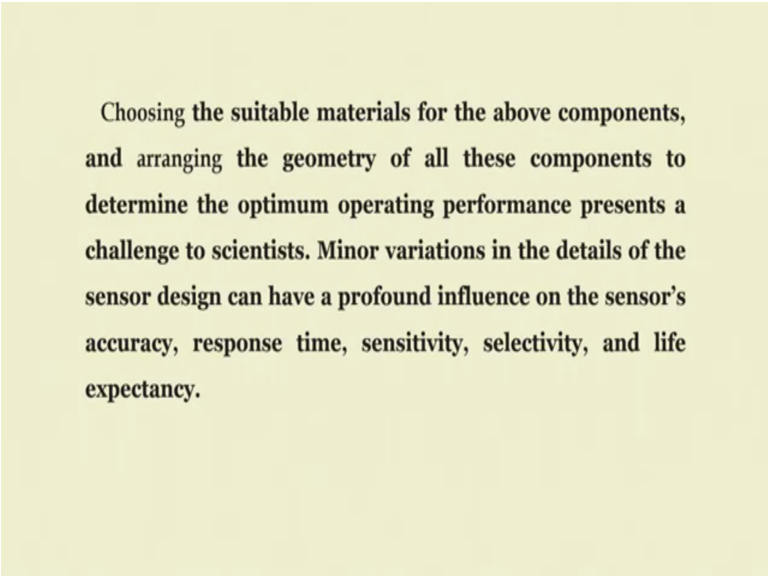

So, here is an important lesson for us that filters are very important not only for removing the unwanted materials, but also to remove the finer and coarser materials. To remove them it is important for us to choose the correct filter. And then, choosing the suitable materials above the components for the above components and arranging the geometry and all it becomes to determine the optimum performance etcetera is a challenge to scientists and the design engineers.

So, minor variations in the details can have profound influence on the quality of the sensor that is potential and other things remain essentially same that is accuracy, response time, sensitivity. All these things will be dependent upon only upon the finer variations of the sensor material. So, we will continue our discussion on the sensors about their chemical reactions that takes place in our next session.

Thank you very much.