Electrochemical Technology in Pollution Control
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Lecture – 24
Electrochemical sensor 2

Greetings to you, we are talking about the Electrochemical sensors. In the last class I had initiated a discussion on major components of an electrochemical sensor, I had told you that a gas permeable membrane is required in a electrochemical sensor for gas.

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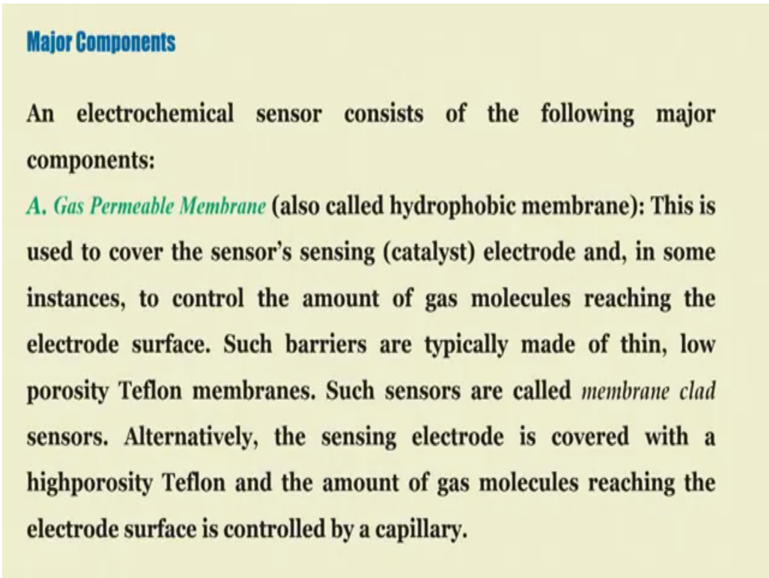

So, it is also it has to be a hydrophobic membrane, that is to cover the sensors sensing electrode and in some instances to control the amount of the gas molecules reaching the electrode. Such barriers are typically made of thin low porosity Teflon membrane and some other biological membranes also can be used. And, this hence they are since only membranes are used for such purposes they are all called as membrane clad sensors.

Alternatively the sensing electrode is covered with a high porosity Teflon also and the amount of gas molecules reaching the electrode surface is controlled by a small capillary. So, because it is meant for gases and such sensors are normally referred to as capillary type sensors. Besides offering mechanical protection to the sensor, the membrane normally performs additional function of filtering out unwanted particulates and other gases etcetera.

Selecting the correct pore size of the membrane and capillary is very important in all gas sensors. Actually, what is to be controlled is the pore size that has to be large enough to allow gas molecules to reach the sensing electrode. And, the pore size should also prevent liquid electrolyte from leaking out or drying out the sensor too quickly.

So, quite often we use zeolites; zeolites are known to have very specific pore size that can allow known gases of ah particular type molecular size to pass through the membrane. And, we also discussed about the electrodes.

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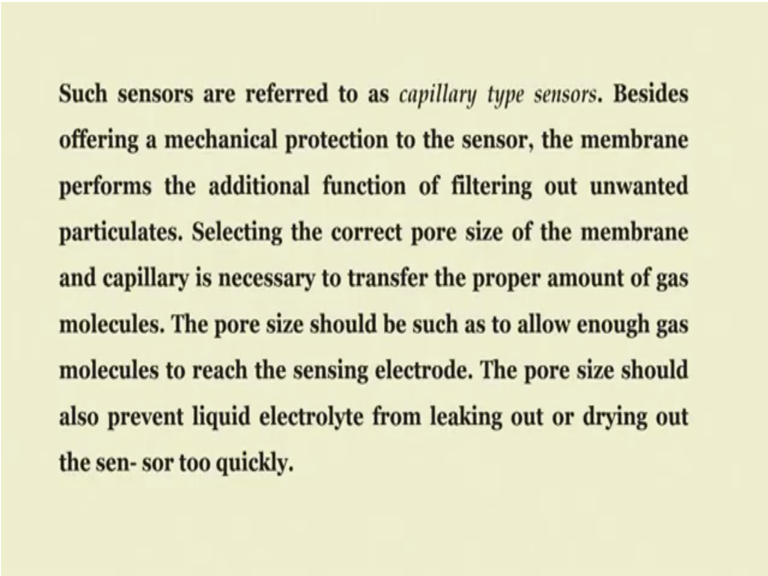

Basically, this electrode selection is a very important it is catalyzed which performs the half-cell reaction for a long period of time. Typically, it is made from noble metal, because through noble metals continue to work for long time without poisoning. What are the noble metals normally we employ? They are all platinum, gold, silver, and sometimes copper even the copper is not a noble metal, it is a coinage material.

So, depending on the design of the sensor all three electrodes can be made of different materials to complete the cell reaction; that means, the electrode reaction could be one of it is first kind, second kind and third kind both all the three. So, first kind means electrode in contact with it is own solution, second one is electrode with a contact with it is a um insoluble salt, solution, sparingly soluble salt.

Third is totally noble metal with two different types of solutions that in here in this case in sensors, we all call it sort of reference solutions. The third part is electrolyte, the electrolyte is of course, a solution of the salts, it must facilitate the cell reaction. And, carry out the ionic charge across the electrode efficiently that is all it is job.

It must also form some sort of a stable reference potential with the reference electrode and be it must be compatible with the materials used within the sensors. It must be compatible with Teflon, it must be compatible with the cell membrane and it is other salts.

So, like that there are polypropylene, propylene, nylon, any other material that it should whatever we use, it should be compatible. So, if the electrolyte evaporates too quickly then what happens? If, the electrolyte goes the sensor will not operate.

So, the sense it is important that we maintain the electrolyte in a solution and what better way for us to retain it as a solution. If, it is if the solution is too dilute, water will evaporate and concentrate and then there will be changes in the electrical signal.

If, it is too concentrated then again the transport of the ions and other things will be affected owing the viscosity. So, it must be fairly not too dilute, not too concentrated, that is the requirement. Sometimes, to avoid all these things we use gel gels. So, that it retains it is a liquidous character and not very viscous also.

So, for all practical purposes gels are the most favored electrolytes in most of the electrochemical sensors. So, next comes the filter, we have also, we had discussed this also to some extent. So, a scrubber filter is installed in front of the sensor, to filter out and there is a there are a number of selection of a filters, each with different degree of effectiveness.

Most commonly used filter medium is activated charcoal. Activated charcoal has got the property of high surface area and it can react with number of polar and nonpolar substances, it can adsorb and then let out only the substances which we want to measure.

So, the activated charcoal filters out most of the chemicals with the exception of carbon monoxide and hydrogen gases. By properly selecting the filter medium an electrochemical sensor can be made more selective also to it is target gases, quite often I have found personally, that people who use electrochemical sensor believe in the efficiency of electrochemical sensors too much and do not even bother about the interferences, but actually everything is chemically governed.

So, one has to really worry about electrochemical sensors being going out too try they are all mechanical defects. Sometimes, they go to try etcetera, sometimes there may be other gases, which may react giving you higher or lower results. So, that also is not desirable basically.

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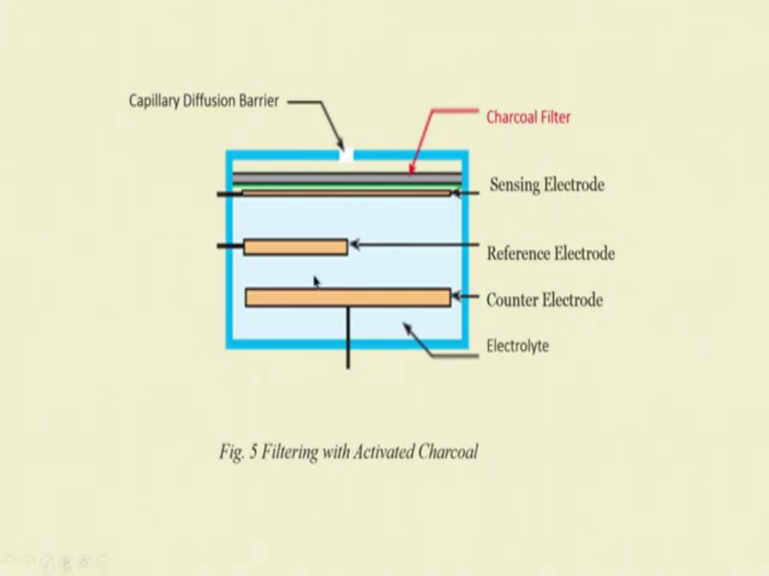

Fig. 5 Filtering with Activated Charcoal

So, I have shown you this figure and then I had stopped here. Maybe, one more slide I had shown you, but basically this design helps you to serve to serve the requirement of an electrochemical sensor with activated charcoal. So, here I have a black piece that is a charcoal filter. And, then here is our capillary diffusion barrier, all the gases and other things will diffuse through this, come in contact with this charcoal filter and then I have a sensing electrode.

So, whatever is not adsorbed will be coming onto the sensor. And, then I have a reference electrode and a counter electrode and everything is filled with the electrolyte. So, this is the typical construction of a sensor this is the electro typical construction of a sensor.

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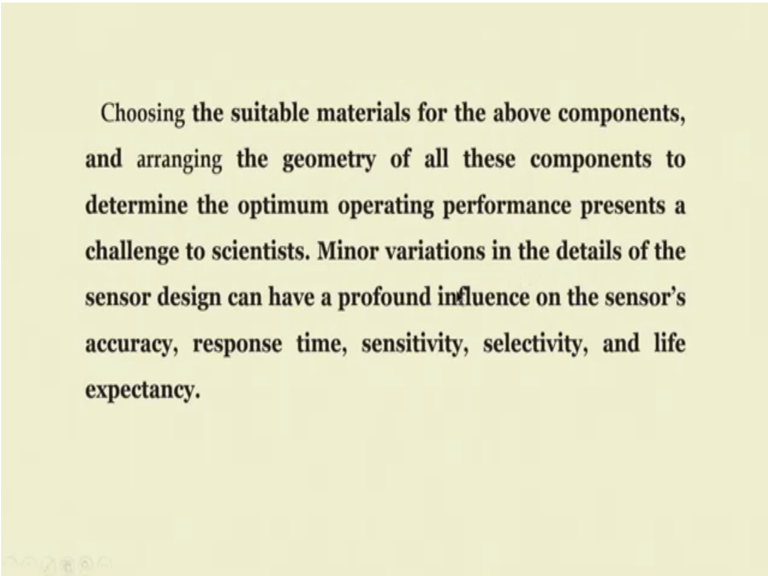

So, choosing the suitable materials for the above components and arranging the geometry of all these components to determine the optimum operating performance present itself is a separate challenge to the scientists. There are that is why there are so many variations in the sensor design, many people may change the design particularly, because chemistry is same.

So, from a trade point of view or from the business point of view it makes sense to change minor components and that provides for minor variations in the details of the sensor design. To have a profound influence on the sensors accuracy response time, sensitivity, selectivity, life expectancy, and then quite often we worry about the efficiency also and interferences. We do not write all these things here, because the chemistry remains the same whereas, physical parameters like this accuracy response time sensitivity, they all change quite often.

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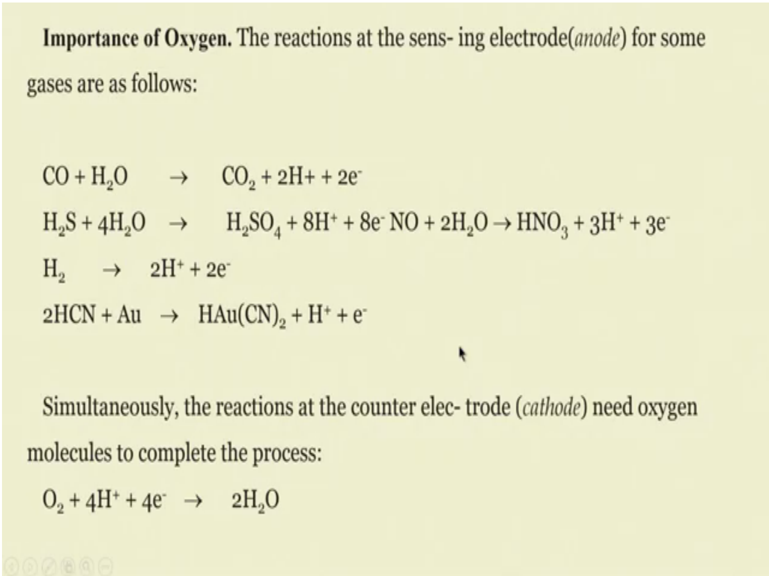

So, again the chemistry is the trick involved here and we worry about oxygen. So, we know all these reactions that happen at the electrode. Especially, for some of the gases including carbon monoxide H 2 S, H 2 and HCN. I have written here some of the equations, that reactions governed by the presence of other components.

For example, if there is carbon monoxide and water vapour is there, we will definitely end up with having a carbon dioxide and hydrogen ions plus 2 electron, this is a very very well-known reaction. And, if you have H 2 S and water there is there will be formation of H 2 SO 4 plus 8 H plus plus 8 electrons, if you have nitrous oxide, nitric oxide, it will react with 2 H 2 O giving you HNO 3 and 3 hydrogen ions. And, if it is only C H 2 then hydrogen molecule itself can dissociate to give you H plus plus 2 e minus.

These are all the electrochemical reactions; basically you have not much control over such reactions. And, another important reaction is HCN. If, you want to monitor cyanide gas, then the best way is to put a electrochemical sensor containing gold. Gold will react with HCN to form auro-cyanide complex that is HAu CN twice and releasing one hydrogen and electrons.

Simultaneously lot of reactions at the counter electrode that is cathode need oxygen molecules to complete the process. So, wherever there are H plus ions, we need the here in all these reactions there are H plus ions. Now, 2 H plus here, it is 8 H plus, here it is 3 H plus, here is 1 H plus H plus means protons basically.

So, wherever protons are generated, if there is oxygen we will have this reaction that is O 2 plus 4 H plus plus 4 e minus going to 2 H 2 O. So, in all sensors water is the enemy. Enemy for all electrochemical sensors is water.

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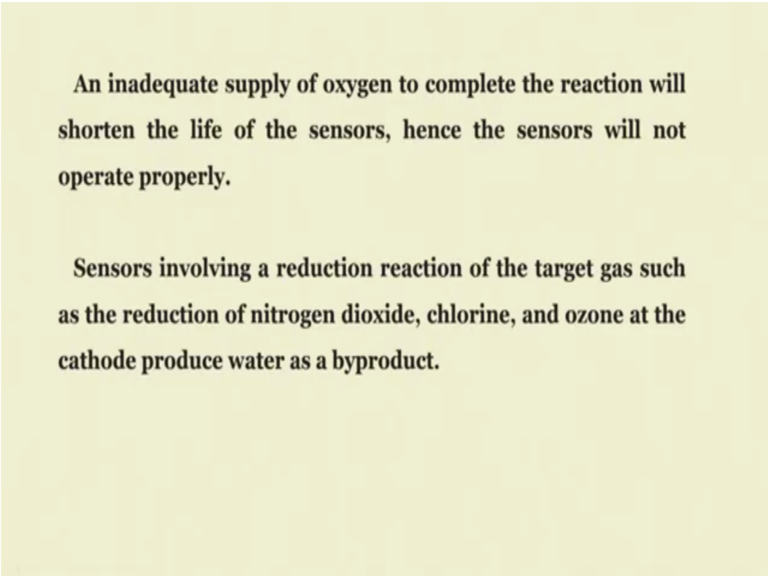

So, in inadequate supply of oxygen means, the reaction will shorten. And, the life of the sensors the is gone. So, the sensors will not be operating properly. If, there is oxygen and there is water, then the all other reactions what I had shown in the previous slide, they will start operating and we will have problems here.

So, sensors basically involving a reduction reaction of the target gas. What would be the target gas in most of the cases? If you are monitoring air environment, we would be having nitrogen detection, we will be requiring detection for nitric oxide NO 2, H 2 S sulfur dioxide and such things, apart from a sensors required in specific reaction.

For example, if you have a petrochemical complex around then; obviously, one would like to have a gas sensor. That is a hydrocarbon sensor, one can have a fire sensor, smoke sensor and several other thousands of sensors are there, which need to be fitted at appropriate places for monitoring the environment.

So, sensors involving a reduction reaction most of the things like SO 2, NO 2 etcetera, they are all reduction reactions. They target the target gas the these are the anyway they are here anyway. So, nitrogen dioxide, chlorine, ozone they all produce at the cathode water that comes as a byproduct.

So, wherever there are oxygen atoms in the analyte there will be water as a by-product. So, the typical reactions will be going on it would not dry out, that is what I am trying to tell you.

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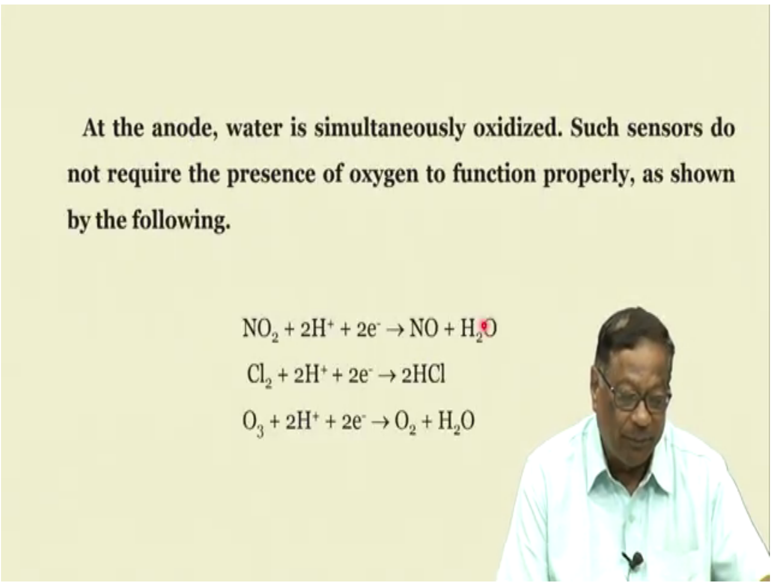

So, at the anode very simple, water is simultaneously oxidized. Such sensors do not require presence of oxygen also is not it. Because, the simple reactions will happen for example, if, I have NO_2 and 2H plus is there, we have it is a 2 electron system producing nitric oxide. And, just for your kind information NO_2 here the valency of a nitrogen is 4 and the reduction reaction with hydrogen occurs giving you NO, that is valency of 2. So, 4 to 2 valency reduction is possible in the case of nitric oxide.

Suppose, I have chlorine; chlorine also gets should get reduced. And, what product it will form? You may look at the reaction where I am showing, but it is better to remember addition of hydrogen is reduction. So, chlorine will react with water add a hydrogen add enough electrons to produce a molecule with no charge that would be hydrochloric acid.

So, we can try ozone right typical reactions and then we get water and oxygen, very simple basic reactions. And, one does not have to know a lot of chemistry to imagine, these reactions occurring at the electrode either it is it can be anode or at the cathode, depending upon the type of species that is produced in the electrolyte.

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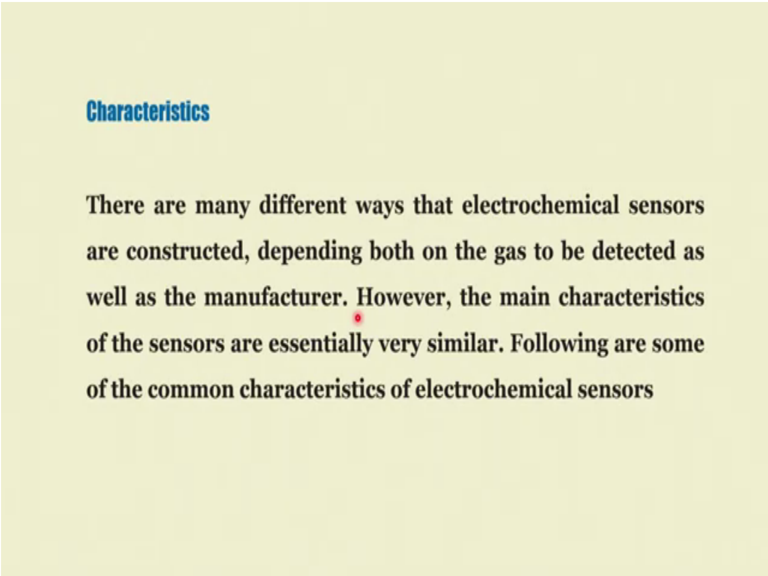

So, here are some characteristics, that electrochemical sensors are constructed and depending on the gas to be detected as well as that of the manufacturers. We generally list the characteristics and the main characteristics are essentially very similar. And, three electrode sensor for example, every sensor will have a three electrode system.

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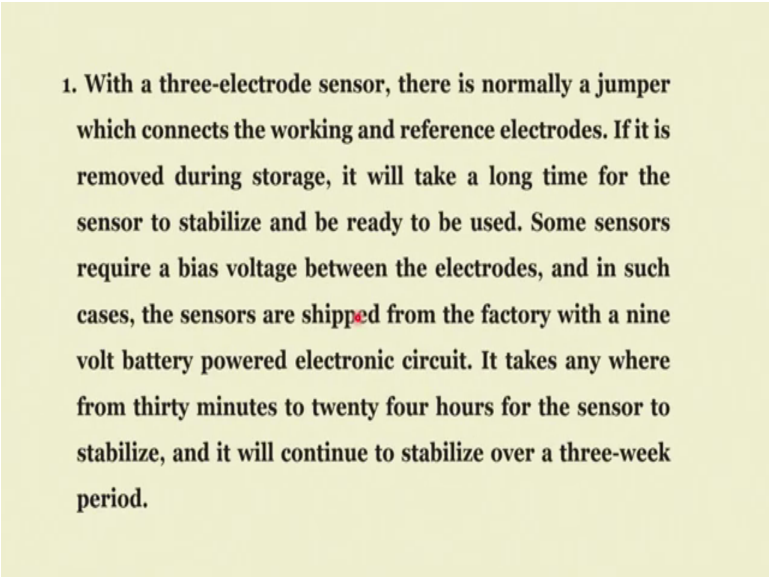

So, there is normally a jumper, which connects the working and reference electrodes I should go back to show you what is a jumper and let me try.

So, here you can see a jumper here connection a small connection you will see in this area. So, if the jumper is removed, it will take a long time for the sensor to stabilize. And, it will be long time before it is used. Some sensors require a bias voltage jumper means basically a short smart working connector connected with a wire or something.

So, we have the bias voltage, we just give a push a little bit, we just give a push a little bit and then the a electrochemical sensor will start working. And, in such cases sensors are shipped from the factory with a 9 volt battery powered with electronic circuit. Automatically, it will come you do not have to worry about, what type of a battery I need etcetera they come along with the sensors.

So, when you are purchasing, they will say yes it is a bias voltage required sir, we are providing the battery to give the initial impulse. So, it takes anywhere from thirty minutes to twenty four hours for the sensors to stabilize in such cases and it will continue to stabilize over a three week period. So, during that time you cannot use the sensors very efficiently.

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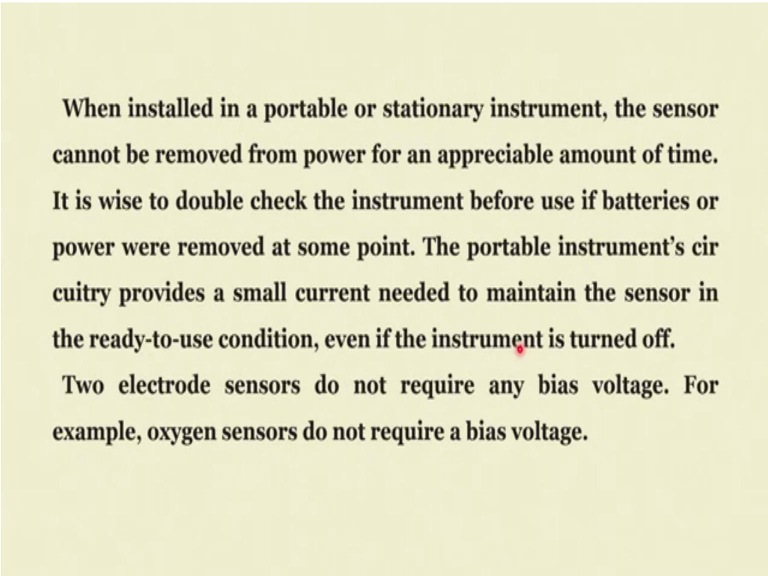

The when installed in a portable or stationary place, the sensor cannot be removed from the power source for an appreciable amount of time. This is very common sense statement. Actually, there is nothing technical about this, it is wise to double check the instrument before use, if the barriers or power were removed at some point.

So, the portable instruments air circuitry normally provides a small current needed to maintain the sensor in the ready to use condition that is very important. A small amount of current is needed to maintain the sensor, even if the instrument is turned off. So, some residual current will always be flowing in the sensor.

So, the two electrodes sensors do not require any bias voltage two electrode sensors. For example, oxygen sensors do not require a bias voltage, why? Because it is diffusion controlled.

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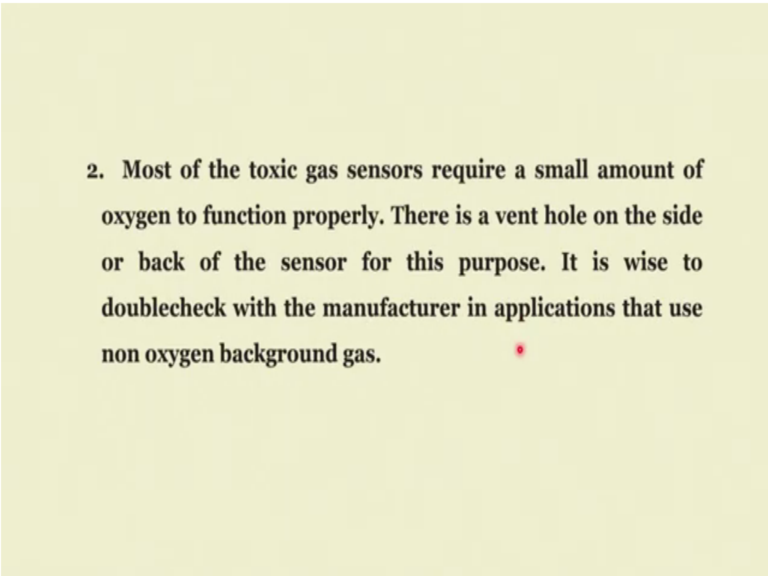

So, if the chemical reaction controlled, we do need a bias voltage, but if it is a directly diffuse diffusion based, then we do not need a bias voltage, because the equilibrium will be automatically established the moment you start the operation of the sensor. But, if it is bias condition, then we have to wait for few days until the sensor starts working properly.

So, most of the toxic gas sensors usually, they require a an amount of small amount of oxygen to function properly. So, there will be a vent hole provided on the side or back of the sensor for such purposes. It is wise to double check with the manufacturer in applications, that use non oxygen background gas..

So; obviously, if you do not see a small hole vent hole then you should check with the manufacturer, whether it is safe enough, because the non-oxygen background gas it may not it may or may not be able to sustain.

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3. Electrolyte within the sensor cell is an aqueous solution separated by a hydrophobic barrier which will not allow the aqueous solution to leak out. However, water vapor can pass through, just as other gas molecules can. In high humidity conditions, prolonged exposure can cause excessive water to build up and create leakage. In low humidity conditions, the sensor can dry out. Sensors that are designed to monitor high gas concentrations have less porous barriers to limit the amount of gas molecules that pass through, and therefore are not affected by the humidity as much as sensors that are used to monitor low gas concentrations, which have more porous barriers and allow a more free exchange of water molecules.

So, coming to the third characteristics, electrolyte within the sensor is an aqueous solution separated by a hydrophobic barrier. Again, I should go back at this stage to show you that electrolyte, but I hope you will be able to remember, the blue solution that is in which all the three electrodes are in contact, in the previous picture only you can go back and now I will check.

However, the water vapor can pass through all the three electrodes, just as other gas molecules can. In high humidity conditions, prolonged exposure to such conditions can cause excessive water build up and create leakage. A very real danger and low humidity conditions the sensor can dry out, that is also possible.

Normally, sensors are designed to monitor high gas concentrations having less porous barrier. Why high gas concentrations? Do not require very high gas passage, you understand. The, if a gas is being produced in large quantities I need to take out a very small portion of the gas, because the gas will be almost pure 99.99 percent etcetera.

So, the sensors that are designed to monitor high gas concentrations have less porous barriers, because it can just pass through, the electrode. And then the they are not affected by humidity, because the residence time of the gas molecules in the sensor is very less.

So, as much as ah humidity; as far as humidity is concerned, they do not have a big role to play in high gas sensors; high speed gas sensors. So, they are used to monitor low gas concentrations it is the other way round, we do need a porous barrier, because gas has to pass through maybe concentrate to some extent to the minimum detection level and then show some sort of response.

So, such porous barriers allow a more free exchange of water molecules also. The bigger the pore size more will be the water passage also through the barriers, that is not a highly desirable again. So, one has to really worry about different aspects of a pore size and other types of efficiency, especially in sensor design. Now, regarding pressure and temperature, that is another important aspect the one has to worry about in the sensors.

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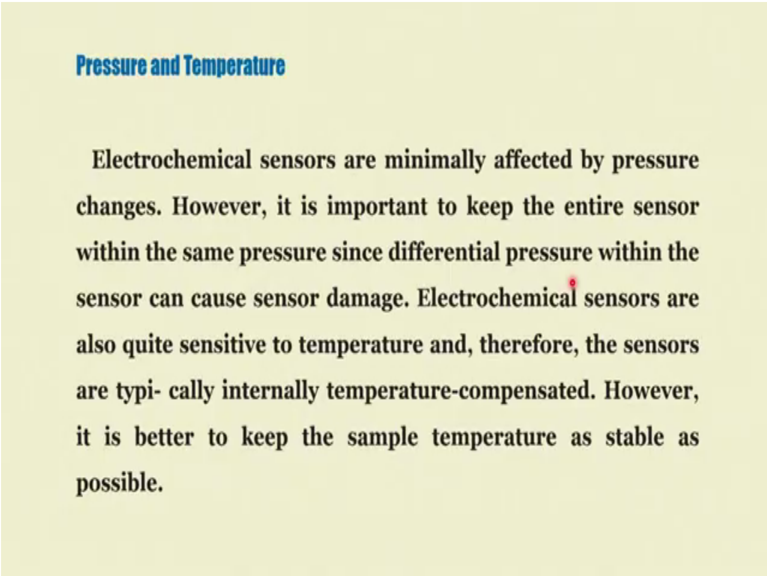

So, electrochemical sensors are minimally affected by pressure changes. Hardly, because you know they all operate most of the time in a normal temperature and pressure. It may be higher than the room temperature or in particular places or not, but they are not produced under any special environment no, normal room temperature and pressure in summer it may be temperature may be up to 35 to 40 range should be good enough and pressure of course, it depends upon the height elevation, seacoast there will be more pressure and higher altitude there will be less pressure.

Either way, temperature and pressure do not have much market effect on the accuracy of the sensor. Because, basically it is a not a regular change that happens and typical weather conditions are maintained over long periods of time.

So, electrochemical sensors are also quite sensitive, but they are sensitive to temperature why? Think about it electrochemical sensors are sensitive to temperature. We have the basic reaction if you remember Nernst equation, you will automatically remember, that the electrochemical sensors have got to be sensitive to temperature, that is inversely proportional R T directly proportional to temperature not inversely, it is directly R T by N F.

So, temperature comes in the numerator; obviously, there will be higher signal if the temperature is increasing at room temperature. And, normally we always sense, that whenever higher temperatures are involved the response is faster, and response is higher, and the sluggishness is very less in the sensor. So, the sensors are typically internally temperature compensated.

Suppose there is a 10 degree centigrade difference between winter and summer, the readings will be approximately double, because the speed of the reaction will be double and that signal will be more disturbed. So, the sensors are typically why go for so much of variation in the signal. Best thing is to have a temperature controlled system, which is internally controlled.

If, the outside temperature goes up the system will reduce the resistance to bring it to the fixed temperature. You can fix the average fix it to average temperature of the summer or a either winter, either summer or winter, you can fix it to any time any for any of the temperature ranges. However, it is better to keep the sample temperature as stable as possible, that is important. Sample temperature once it enters the signal, once it enters the eco sensor, then there is no problem.

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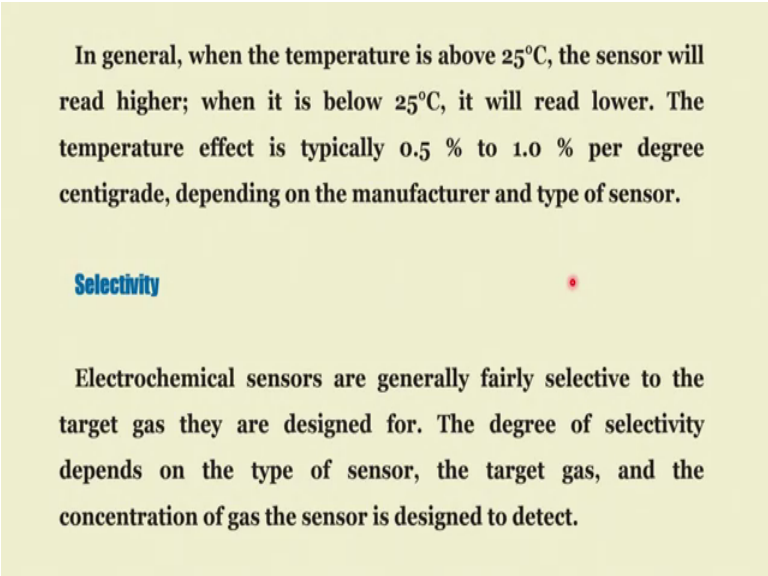

In general we can say that you can set it up to around 25 degree centigrade and the sensor will read approximately fairly good high slightly higher reading, because when it is below 25 degrees it will read lower this thing.

The temperature effect is approximately 0.5 to 1 percent per degree centigrade. So, this can be automatically compensated using the external circuit. And, it depends upon the manufacturer and type of the sensor that we are employing. So, coming to selectivity of the sensors, one can say lot of things. Electrochemical sensors are generally fairly selective to the target gas they are designed for.

Basically, electro chemical sensors means, they are selective. Otherwise, nobody will make the electrochemical sensors by nature most of the electrochemical reactions are selective only, redox reactions, a many of them precipitation reaction they all happen at a particular temperature or at a particular ah reaction conditions, acidity and all other they are mostly selective, very few interferences you really come across in electrochemical reactions except for Carl Fischer or something like that.

For Carl Fischer type of sensors we need to sense only the color of the substance and as an endpoint, that is done electronically that is not so bad. But, the chemistry remains very simple except for reactions such as Carl Fisher, which I have already explained to you earlier in my class. And, regarding the selectivity the degree of selectivity depends on the type of sensor, the target gas and the concentration of the gas sensor in the it is designed to detect.

So, there is not much to say here in expanding this sentence to mean something technically new for you, because we have talked about selectivity we have talked about the target gases. And, we have talked about the concentration of the gas sensor, that is a designed for detection. One can say, if you are producing tons and tons of gases particular case for example, propylene, propane gas, propylene gas, ethylene oxide all these the monomers gases etcetera..

If, they are being produced in large quantities the concentration of the gas required would be very small, that would be in PPM level or parts per trillion level, parts per trillion level quantitation is difficult, but qualitatively one can say it.

I can say that, qualitatively there are many gases, which need to be detected in very small quantities also. We there are many situations where we come across. Especially in food industry and all packaged foods should not have oxygen. So, what is the requirement of oxygen in package foods? It will be about 10 to 15 parts per million volume PPV.

So, out of suppose you have a packet of about 1 kg chips, we do not want oxygen means, the limit of oxygen would be very low only in about half a liter of packet you have to determine. So, much less quantity of oxygen, if we test to pass through FSSAI conditions.

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List of Typical Gas Interference Ratios for CO Sensors

gas	without filter	with filter
H2S	0.3:1	10:1
SO2	2:1	20:1
NO	3.3:1	10:1
NO	1.6:1	10:1
H2	2:1	2:1

The higher the interference ratio, the less effect an interference gas has on the sensor.

So, here is a typical gas interference ratio for CO sensors. What are the gases? For CO sensors we in along with the FSSAI carbon monoxide. Normally, we will have H 2 S, SO 2, NO NO 2 and here it should be NO 2 the second one and H 2 hydrogen gas.

So, H 2 as is 0.3 is to 1 without filter, with filter the range expands to almost 10 to 1. So, 2 is to 1 without filter interference; that means, the CO concentration, if it is half of SO 2 without filter it is, with filter it can be 1 is to 20 ratio, that is SO 2 would be 20 and CO sensor would be 1 only.

And, if you look at nitric oxide, it is 3.3 is to 1 and 10 is to 1, and NO 2 this has to be a NO 2 maybe we will correct it this way, but for your ah sake please correct right now. I would be very happy if you do that, here you right NO 2 NO 2 here ok. I should be able to make it with a pen I think. I will do it right now it has to be NO 2 here.

So, if it is there NO 2 the ratio happens to be 1.6 to 1 and again with filter you have a better selectivity that is 10 is to 1. If, it is hydrogen then it is 2 to 1 and here it does not matter because the hydrogen is the culprit here, because it is a smallest gas molecule that we ever come across. So, the filter is not very effective in removing the hydrogen.

In all these cases these carbon monoxide is a having a different diameter, I mean different diameter and NO 2 is a bigger molecule nitric oxide is a bigger molecule, SO 2 is a bigger molecule and H 2 S is a bigger, but hydrogen is the smallest molecule. So, the filter is not very effective the in a in the case of H 2.

So, one has to be a little worry about interpreting such results. The higher the interference ratio less effect on an interference gas has the on the sensor, that is the bottom line.

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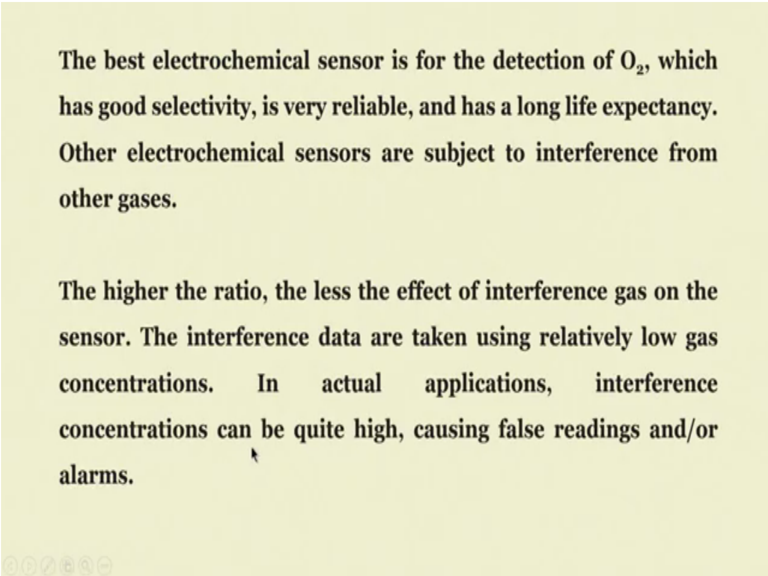

So, the best electrochemical sensor is for the detection of oxygen, which has good selectivity is very reliable and has a long life expectancy. Oxygen detection I have been telling you, that most of our FSSAI. We want them to be 15 PPV parts per in terms of volume 15 parts per million volume PPMV. And, other electrochemical sensors are also subject to interference from other gases.

The higher the ratio less is the effect of interference gas on the sensor. So, interference data are taken using relatively low gas concentrations only. In actual applications they can be quite high causing false readings or false alarms also.

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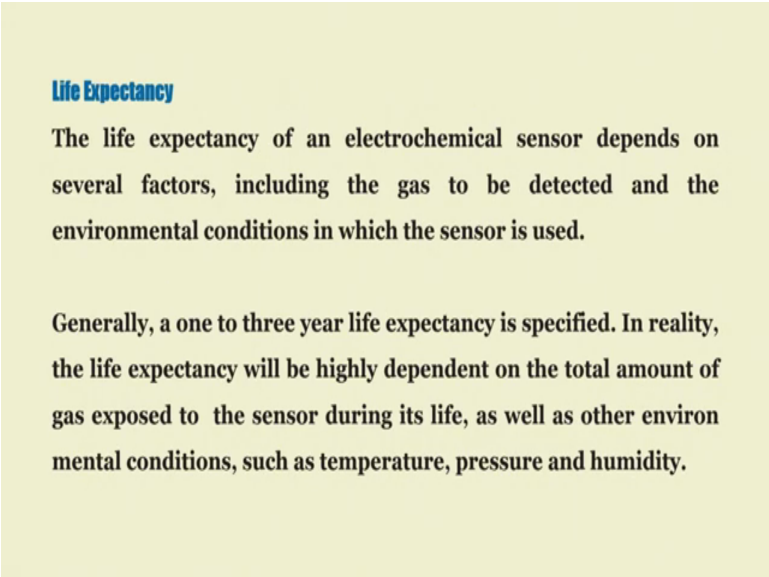

So, what is the another parameter that, we have to worry about the sensors is the life expectancy. So, the life expectancy of an electrochemical sensor, normally as I told you that it is depends upon several factors and including the gas to be detected and the environmental conditions in which the sensor is used. Sometimes, very harsh environmental conditions require frequent removal or frequent substitution of the sensors.

Generally, one to three year life expectancy is specified. Depends upon the manufacturer also, in reality life expectancy is highly dependent on the total amount of the gas exposed to the sensor during it is life, because there will be something like ah a an effect, which is a tiring the sensor will get tired of doing it is duty. So, that only reduces the sensor response ah.

So, other environmental conditions such as temperature pressure and humidity also play a very important role in deciding the life expectancy.

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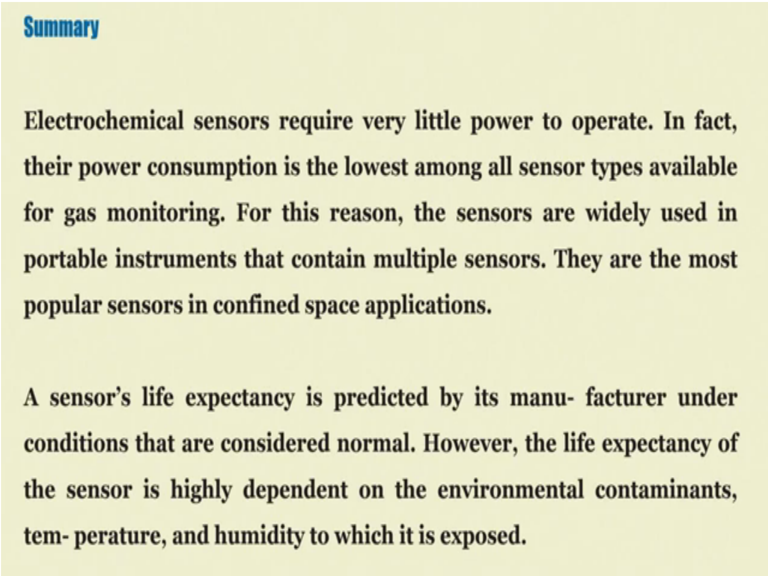

So, in summary what I can say is electrochemical sensors require very little power to operate. Their power consumption is the lowest among all the sensor types available. And, for this reason sensors are widely used in most of the portable instruments that contain multiple sensors. They are the most popular sensors in confined space of applications.

A sensors life expectancy is normally predicted by it is manufacturer under conditions, that are specified. Suppose you change the conditions, there will they will nobody will to give you the guarantee of having a sensor sir our sensor is not working. So, he will never give a guarantee.

So, he will say I will give you minimum 1 year guarantee sir after that it is your luck, how long you will operate?

However, the life expectancy of the sensor is actually dependent upon the environmental contaminants, that we should understand very clearly, it is the temperature, pressure, humidity and all those things. The, because the material through with which it is constructed can get affected and go bad, instead of the sensor membrane or something like that. Because, under high heat conditions etcetera the electrodes will corrode anyway.

So, that brings us to the completion of the discussion on electrochemical sensors and we will move on to the next topic that is electroplating. Thank you very much and we will continue our discussion on electroplating in the next class.

Thank you.