**Physics of Renewable Energy Systems**
**Professor Amreesh Chandra**
**Indian Institute of Technology, Kharagpur**
**Lecture 39**
**Microbial Fuel Cells**

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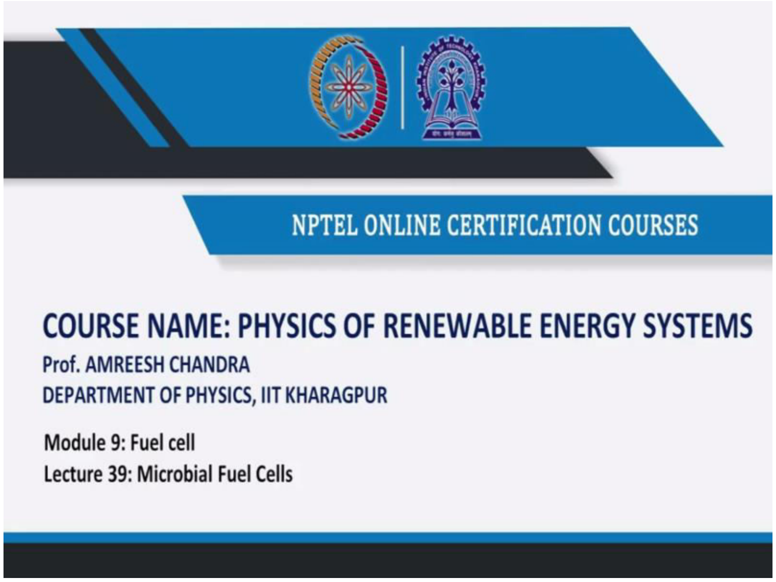


Welcome to the third lecture on fuel cell. And today, we will talk to you about a kind of fuel cell that is microbial fuel cells, which can be very useful for country like India, where we are looking for the solutions of wastewater treatment and also, we want to cater to the fast-growing demand for electricity. So, this technology as of now, although it is a low power device, but as research progresses and more and more knowledge is attained in this field, you will find that this kind of fuel cells can become extremely useful for India.

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Because microbial fuel cells can simultaneously treat the wastewater while delivering electrical output or electricity. As of now, it is a low power device. So, this is there that it is a low power device as of today, but the future prospects for this technology is quite bright. And if more research activities are carried on, then hopefully in a decade or so, you will find microbial fuel cells readily available in the market and you can use them for various applications.

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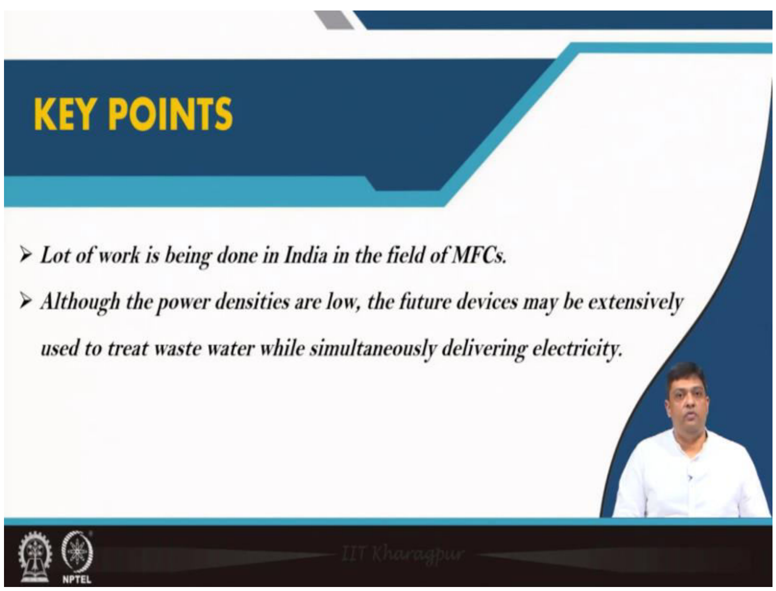


Why am I focusing on MFCs? Generally, if you look into fuel cell-based lectures or courses, you will find people talk about the alkaline fuel cells or the PEM fuel cells or SOFCs. But I am focusing on MFCs because a lot of work is being done in India in various Institute's across the country and we are considered to be one of the leading nations where the work on MFCs is going on.

And therefore, I am focusing on MFCs and if anyone gets interested, then you can also contribute and by joining the team in any of the places where the work is going on, you can contribute in the development of this technology where you can simultaneously treat waste water while obtaining electricity from the device.

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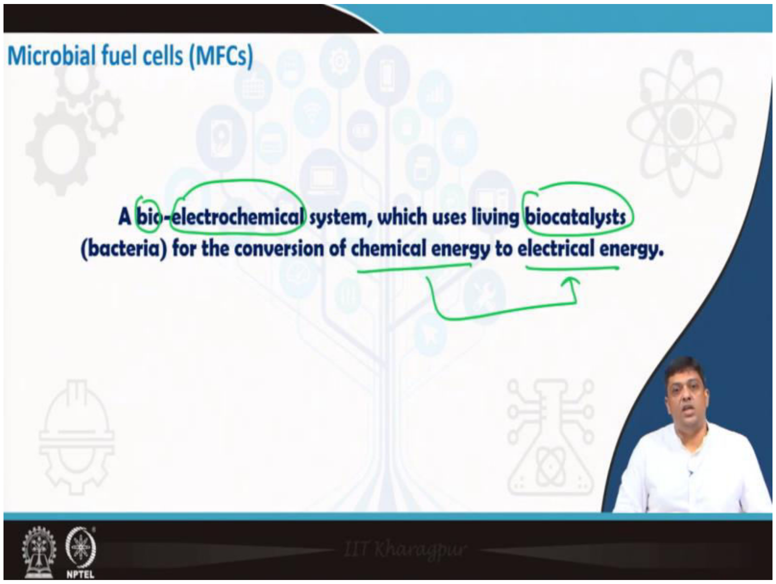


Broadly speaking, a microbial fuel cell is a bio electrochemical system which uses living bio catalysts such as bacteria for the conversion of chemical energy to electrical energy. So, you use living bio catalysts such as bacteria, which actually can take part in the redox reactions and then, because of that, you can get free electrons which can pass through the external circuit and you will get electricity.

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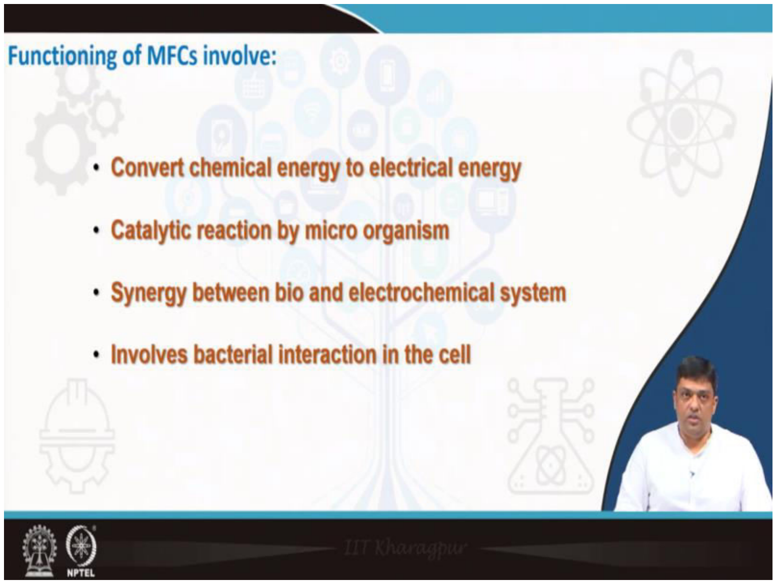


So, the functioning of MFCs involve the conversion of chemical energy to electrical energy, it involves catalytic reactions by microorganisms and you have synergistic combination that is beneficial or advantageous combination between bio and electrochemical systems. Mostly, if you are talking about microbial fuel cells, then you are talking about the bacterial interactions in the cell. If you talk about enzymatic fuel cells then you are using various kinds of enzymes to carry out such activities, but we will focus mostly on MFCs.

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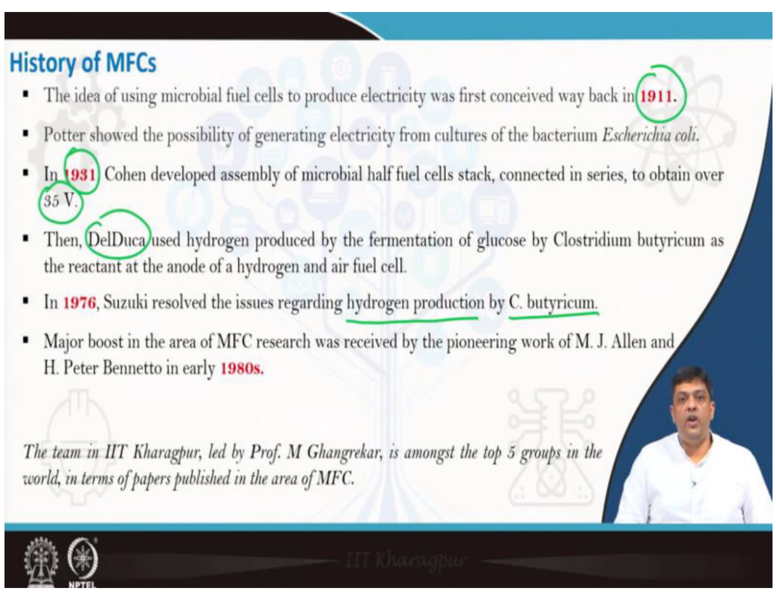

Again, you will see that the concept is more than 100 years old and most probably if you see the literature which is published and documented then probably the first example of a fuel cell using microorganisms to produce electricity was proposed around 1911 by Potter. Where it could be observed that there was an electrical output when you were using the cultures of bacterium E coli.

In 1931, then Cohen developed assembly of fuel cells, half cell, so, they connected half cells and then they made a stack which were forming by the addition of these half fuel cells in series and they could deliver voltages in the range of 35 volts or so. Then came the work by DelDuca, where the fermentation of glucose by Clostridium butyricum as the reactant at the anode of the hydrogen air fuel cell you could obtain the hydrogen as the output.

In 1976, Suzuki resolved this issue and gave an explanation of the functioning of this fuel cell and the issues regarding the hydrogen production by the bacterium could actually be answered. Then in 1980s, they were worked by Allen and Bennetto and the work is going on, there are various teams in Europe, in Northern America, in Australian subcontinent in Asia, in China and India, mostly you find a lot of work is going on.

And there is a team in IIT Kharagpur led by Professor Ghangrekar in the Department of Civil Engineering which is considered amongst the top five groups in the world in terms of papers published in the area of MFCs. So, in India also, there is a lot of work going on and very high-quality work is going on.

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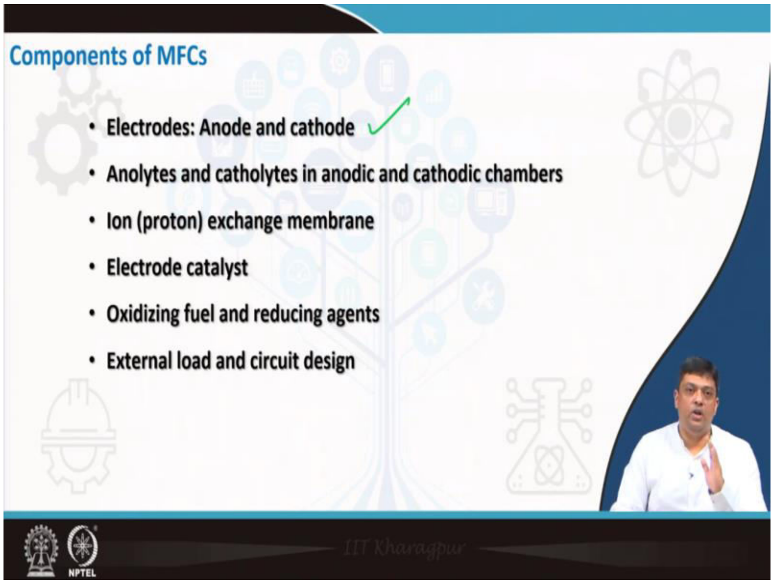


The moment I talked to you about a fuel cell, as we saw in the previous two lectures, what are we talking about? Fuel cells, if you just think what you have learned in the previous two lectures, you will immediately realize that the fuel cell would have various components and the main factors would be defined depending upon the performance of the electrode materials, the electrolyte, the ion exchange membrane and the catalysts. So, this is what you will understand.

If you look into the components of MFCs then again MFCs are fabricated using anode and cathode you have the anolytes and the catholytes right in the anodic and cathodic chamber respectively. Then, you have an ion exchange membrane or a proton exchange membrane. So, if you are looking into a transfer of an ion then you are using an ion exchange or if you are looking at a transfer of H plus then you are talking about proton exchange membranes.

You need to enhance the reaction rate. How will you announce the reaction rate? You are going to use catalysts. So, you will have catalysts as another component which will decide the reaction rates then you have to have electrons then those are obtained using the oxidizing fuel on which the reducing agents are going to work on. And finally, if you want to have electricity, then you have the external load and the circuit design by which you will have the flow of electrons and you will get electrical output.

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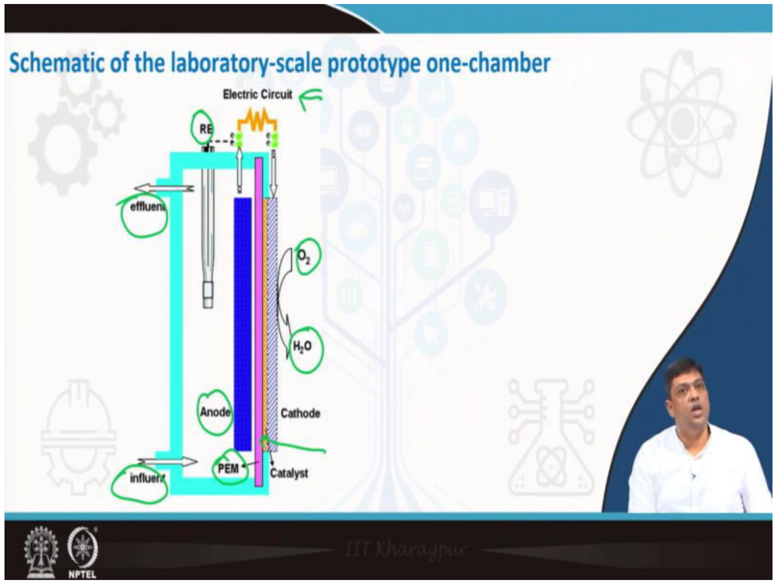


If you look into the design then you have the influent, the effluent you have the reference electrode, you have the external circuit, you have the catalyst loaded electrode. In addition, you have the proton exchange membrane, the anode. We are talking about the half cell. So, then you have the oxygen reacting with the catalysts and at the electrode, electrolyte interface and the output which you have is the water molecule. So, this is what you have as the prototype of one chamber.

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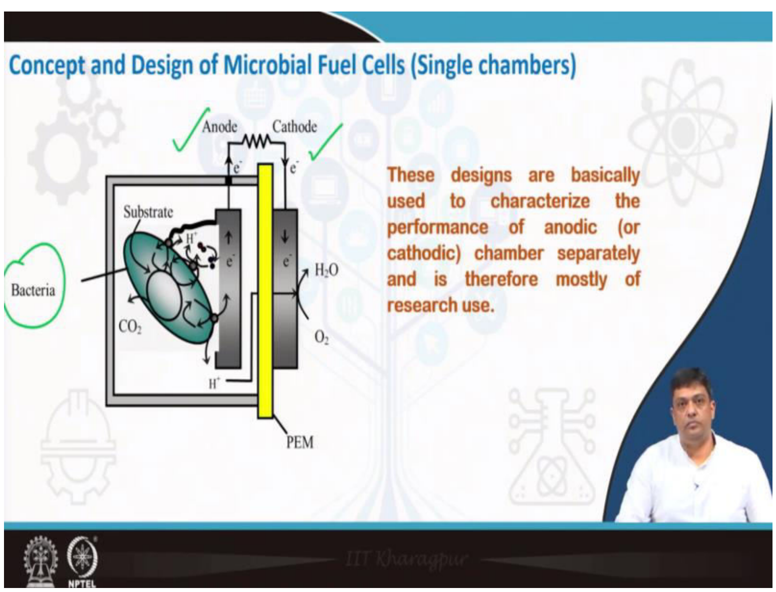

So, if you talk about single chamber fuel cells, you have the cathodes you have the anodes and you have the bacteria which is acting on the influent. What is the influent? Then that is the waste water or you use any solution or any waste stream collected solution where bacteria can act and then they can lead to the generation of electrons. This is what you are looking at.

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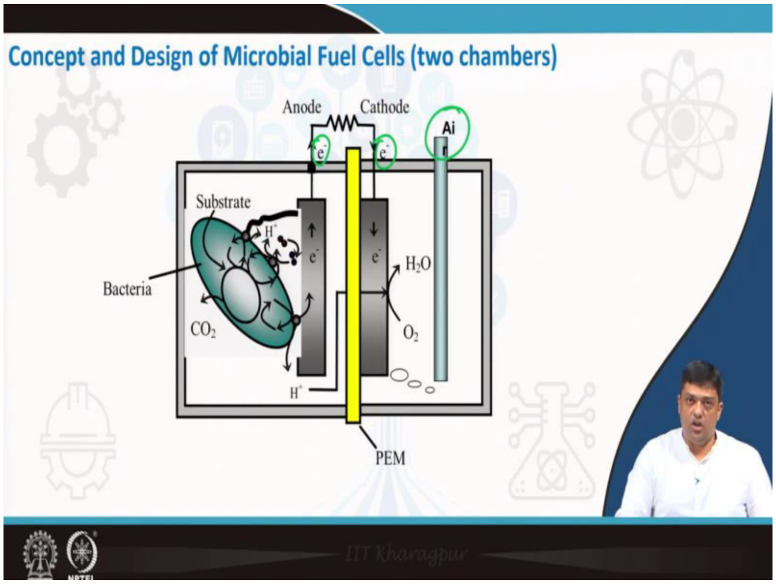


So, if you are talking about the two chamber fuel cells, you are looking at the full cell then you have air by which you are obtaining the oxygen and then you have the interface where the electrolyte is interacting with the electrode and the catalyst loaded cathode and then you have the flow of current. So, the bacteria are actually used to reduce the waste water or the bio-organisms that are present in the waste and then you have the generation of electrons.

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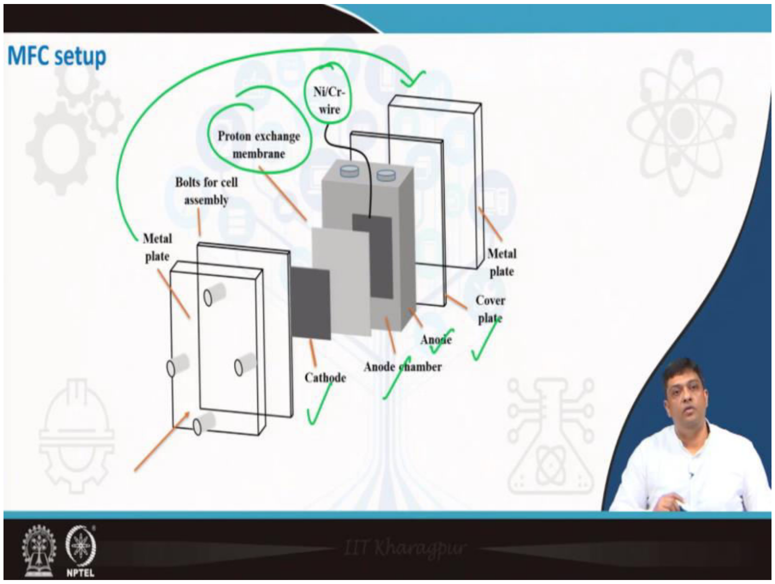


This is a typical construction of a fuel cell. So, if you would like to make a fuel cell, this is the way it is made, you have two metal plates. So, this is the way you will, you can say this is the way you are going to fix the complete setup between the two metal plates. Now, when you have the metal plates, you will also have the assemblies in between so, you have a cathode, you have the anode chamber, then you have the anode, you will cover it from the other side that leads to the plate and then you will tighten the whole setup using the two metal plates.

So, this is like a closed setup. And then you have the nickel chromium wire attached to the anode to extract the charges. You have the proton exchange membrane ensuring no short circuit between the anode and the cathode but allowing the flow of ions or in this point if you are using proton exchange membrane, then H plus. So, this is the typical design of a microbial fuel cell.

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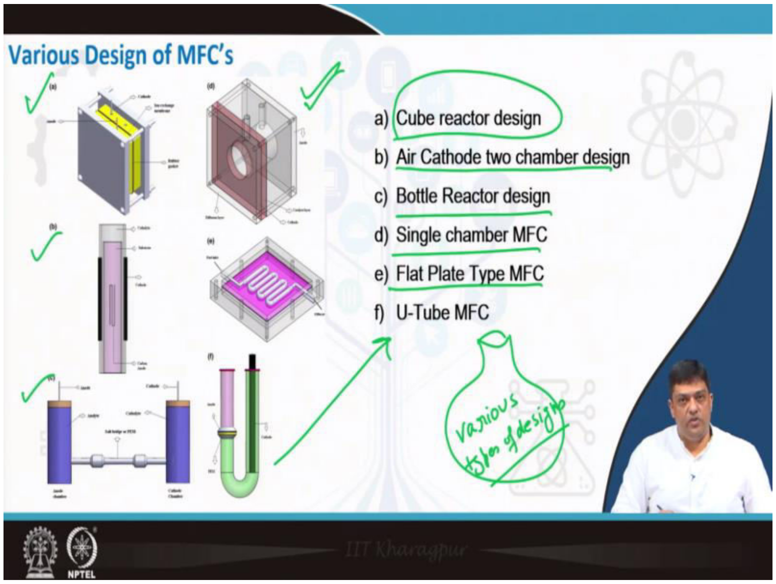


There are various types of fuel cells more so microbial fuel cells, which are used and the name actually comes in from the shape of the reactors. So, how does the MFC in given a, looks like? It looks like a cube reactor. So, it is called a cube reactor design of MFC or cube reactor type MFC. Then you have the air cathode but two chamber design, then you have the bottle reactor design, you have a single chamber MFC.

So, it is one chamber where the whole process is taking place. Then you have the flat plate type MFC and then you have the U- tube type MFC So, depending upon the design you name the MFC. And these are not the only designs which are used, you can make any other design depending upon the availability or the molds which you have. There are people who have actually made MFCs in the shape of earthen pots.

So, you can have various kinds of designs, you can have various types of designs. And it all depends what you want to do design, and what is the availability in the nearby market or in the workshop and based on that you will make the design of the MFC.

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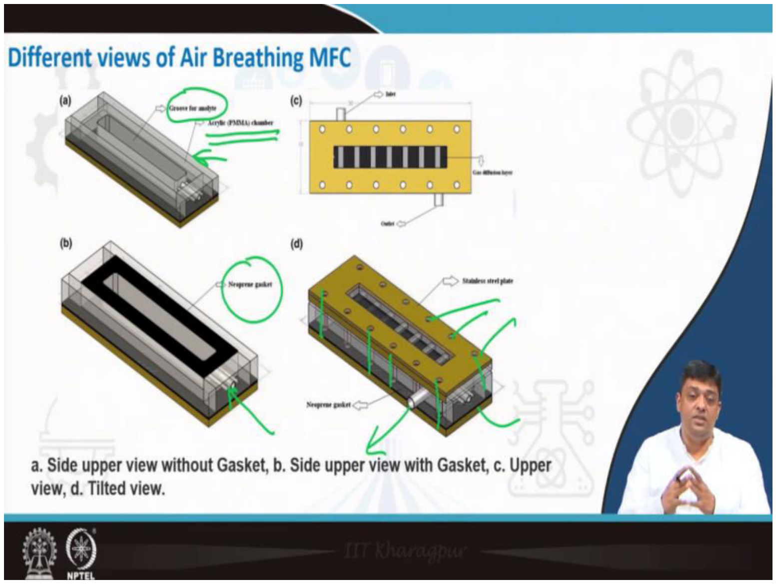


So, if you look into air breathing MFC where you are feeding air so, this is a typical design. What you have? You have the groove in the middle where you will have the anolyte then the whole chamber is actually made using an acrylic. So, you can why am I using acrylic because it is easy to mold and machine the acrylic based chamber.

Then you have the gasket so that there is no leakage, you design the way you are going to allow the stream or the wastewater which needs to be treated to go in and the way it will come out. And then both the sides you have the stainless-steel plate and so that you can tighten the whole assembly as one. So, you can tighten the whole assembly and the screws connect both the sides of the plate and then you can operate this fuel cell.

So, it is very easy to make, the designing is quite simple and machining is also quite easy. And once you make the 3D pictures and give it to your mechanical workshop, they should be able to make an MFC quite easily. If you are able to make anode material, if you are able to make cathode materials, you can have very simple proton exchange membranes or concepts which will allow ion transport and prevent electronic short circuiting, then you can actually make MFC quite easily.

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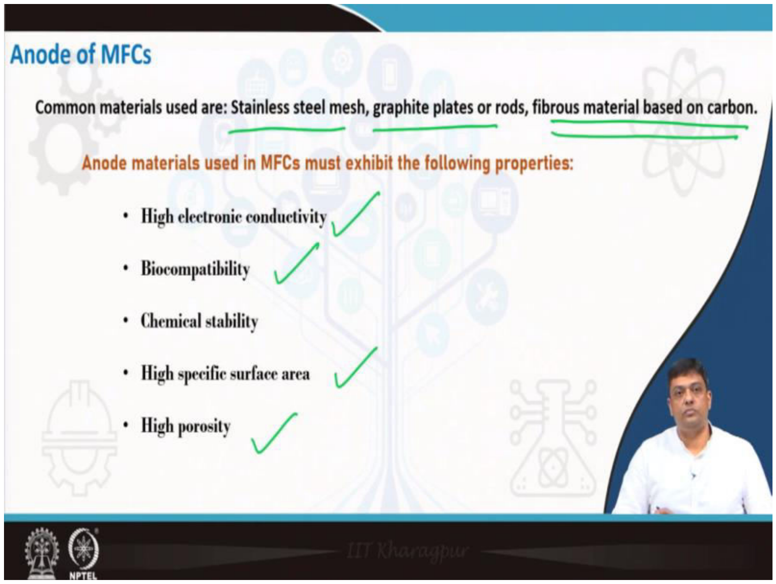


The common materials used in MFCs and let us say in anode side, is the stainless-steel mesh or you use graphite plates or rods or materials which are made up of different forms of carbon. But the properties you are looking at, in these materials are they should have reasonably high electronic conductivity, stability, both in terms of chemical and in terms of mechanical stability, because they will be exposed to harsh or toxic waste waters.

So, they should be able to sustain such kind of environment, it should be biocompatible and the materials which you are going to use the moment I am talking about carbons, then I am already indicating towards the use of high surface area materials which can also have porosity, why porosity we saw in the previous lecture, so, that you allow the inflow of the gas, oxygen if you are talking about or hydrogen.

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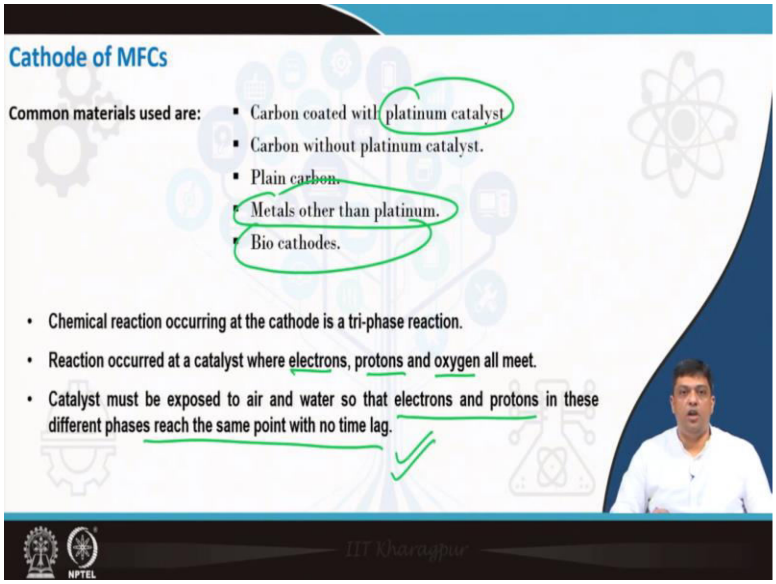


The cathode side, the common materials are based on carbon which are coated with platinum or any catalysts or you can have metals other than platinum which can also have the capacity to act as a catalyst or you can also have bio cathodes. The chemical reactions occurring at the cathode is a tri phase reaction and reactions occur at the point where electrons, the protons and oxygen's all meet.

But catalysts must be exposed to air and water so, that the electrons and protons in these different phases reach the same point with no time lag. So, this is essential. So, you must ensure that the reactants reach a particular point simultaneously otherwise, you will never have a chemical activity taking place. So, that is essential to understand and this is what is meant by the third statement written at the bottom.

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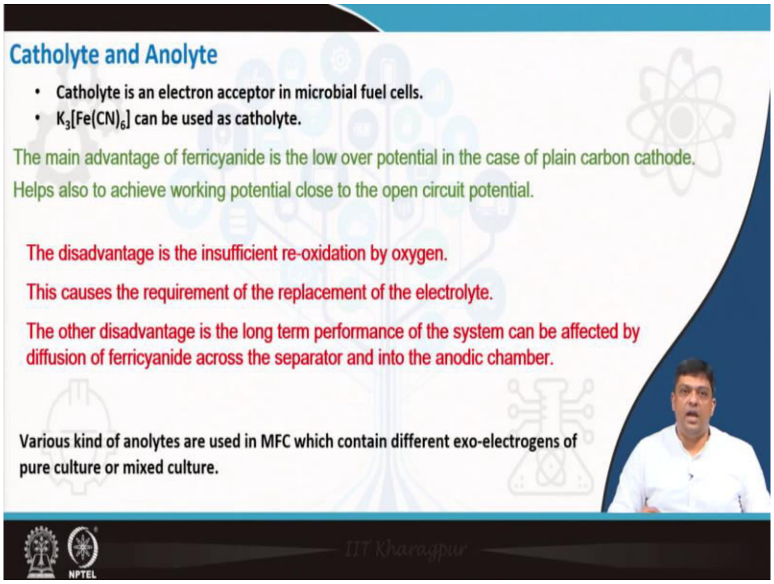


For example, let us take an example of potassium ferricyanide which is one of the commonly used catholyte. What is a catholyte? It is basically an electron acceptors. So, the main advantage of ferricyanide is it is lower potential in the case of plain carbon cathodes, it also helps to achieve working potential close to the open circuit potential or voltage. But there are disadvantages. So, it is insufficient re-oxidation of oxygen.

This causes the requirement of risk replacement of the electrolyte itself because then you do not, you have incomplete reactions taking place and then the electrolyte itself is getting damaged. The other disadvantage is the long-term performance of a system can be affected by the diffusion of ferricyanide across the separator and then that can affect the property of the separator itself. So, the moment I say I have taken an example and there are some advantages and then there are very serious disadvantages associated with the catholyte.

You would say that if that is so, why do not you use different types of anolytes. And that is what is done, that you have various types of anolytes and catholytes which are actually investigated and you make such a combination where you have exo-electrogens of pure culture or mixed culture which can give you the desired performance.

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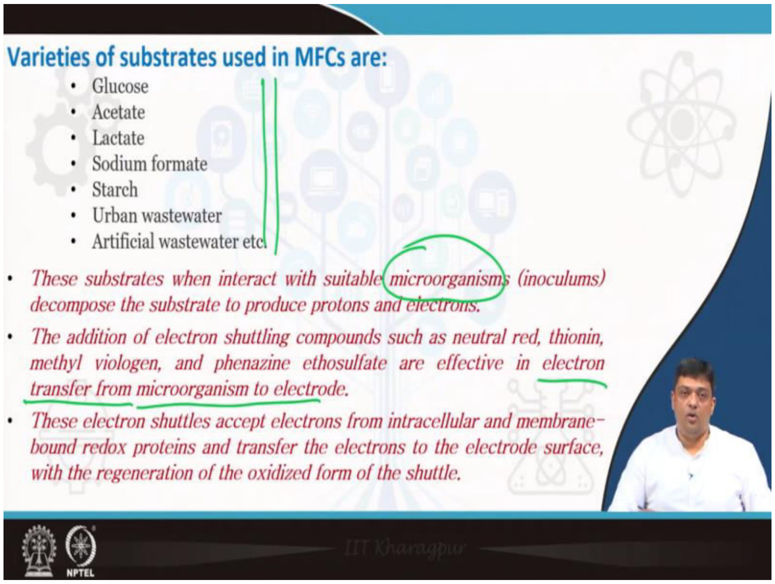


Varieties of substrates which are used in MFCs are substrates which will interact with the microorganisms. And the decomposition of the substrate will lead to the production of protons and electrons. So, you can use glucose, you can use acetates, you can use lactates or you can use wastewater, you can use synthetic wastewater, you can use starch.

So, you have various kinds of substrate on which the microorganisms bacteria's which have the capability to decompose the substrate. Now, in addition to the electron shuttling compounds such as neutral red, thionin or any other material which is going to be used, they have to be effective in electron transfer from microorganism to electrode. So, if you use the shuttling compounds, what are the shuttling compounds?

Now, you have an electrode, now, you have the microorganism which is going to deliver the electron. But how do you connect this microorganism to the electrode? So, then you use electron shuttling compounds, which are able to transfer this electron from the microorganism and then to the electrode and then this electron can move outwards from the external circuit go to the counter electrode and you have the flow of electricity.

So, these electrons shuttles are the ones which will accept electrons from the intracellular and membrane bound redox proteins and transfer the electrons to the electrode surface, with the regeneration of the oxide form of the shuttle. So, you will have the oxide form of a shuttle as the output.

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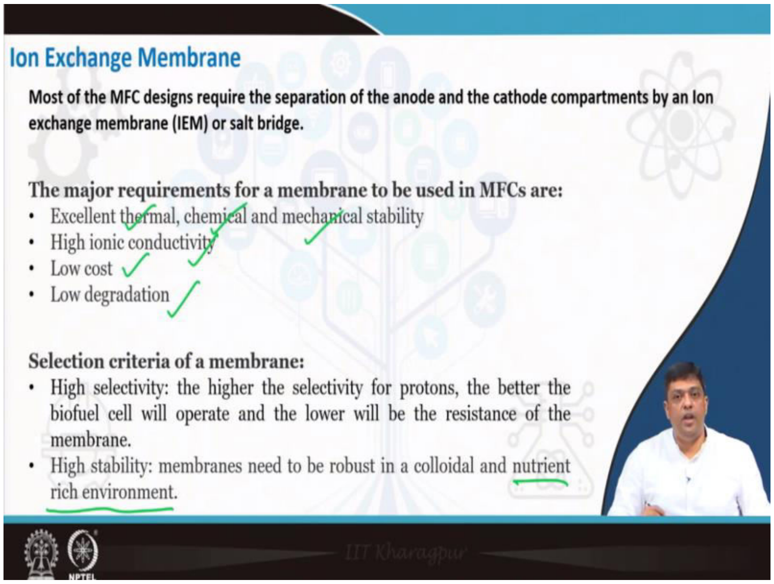


We have already seen the requirement of ion exchange or separator membranes over the last many weeks and the requirement of ion exchange membrane in MFCs are similar to what we discussed in earlier devices. They need to allow certain ions or protons to cross through and they do not allow the flow of electrons across them.

The major requirements for the membranes would be similar to what we have discussed they have to have excellent thermal, chemical, mechanical stability, high ionic conductivity and practically no electronic conductivity, must be economically viable and they should be able to operate for long durations with low degradation. So, how do I choose the membrane?

The way they choose the membrane is that they should have high selectivity and high stability. Selectivity for protons if we are talking about exchange of protons from one side to the other, and stability in terms of the robustness in a colloidal or nutrient rich environment, which can be made using various kinds of elements or ions and they can be quite aggressive and they can harm the membrane. So, they should have stability towards these kind of nutrients.

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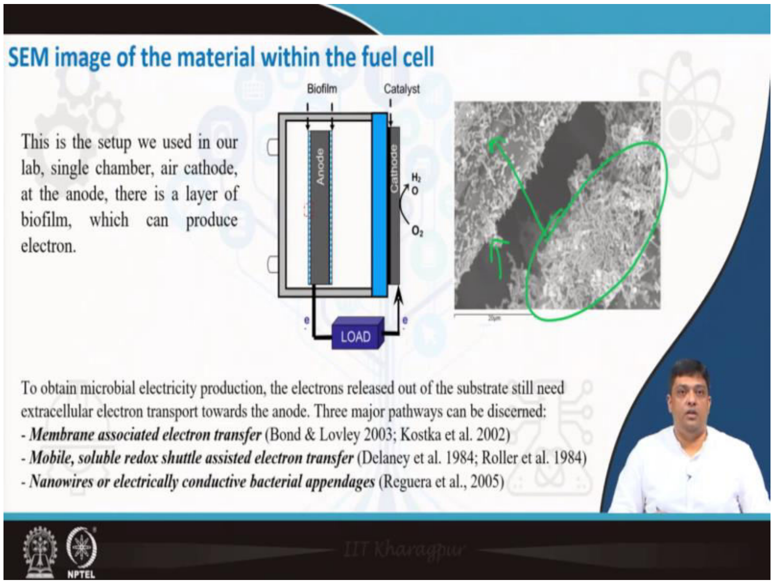


So, if you look into a fuel cell, then it must be clear to you, you will have membrane associated electron transfer, you will have redox shuttles taking part in electron transfer and for that you can use nano wires or electrically conductive bacterial appendages between the microorganism and the electron and that will ensure faster electron transfer.

But if you look into the anode once again, you will see that as you operate the fuel cell what is happening, the biofilm which is forming on the anode will actually change the surface characteristics of this anode. What do I mean? You can see that this is the original anode surface, but because of the operation and you have these micro-organisms or bacterial systems which are available in the solution, they get deposited on top of these anode surface.

And you can clearly see that the performance of the two would be very different, because then the whole structure is covered with different kinds of biofilm, which can have very different characteristics than the ones required for anode. So, these are another major limitations in fuel cells, that the electrode surface gets degraded.

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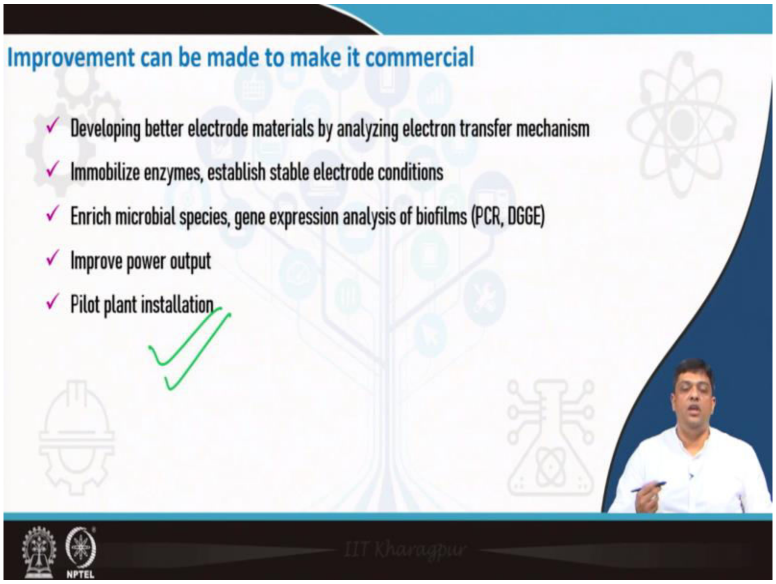


So, for improving the performance and ensuring commercial viability, you must develop better electrode materials, which are also ensuring efficient electron transfer. You should have microbial species which are contributing in the whole process in a way that higher number of charges become available that will lead to higher power output.

And then demonstration of this technology is very important and then you should try to make pilot plant level installation, operate it for a couple of years or months depending upon the timescale you are looking at and then see the performance and then improve the overall system even further.

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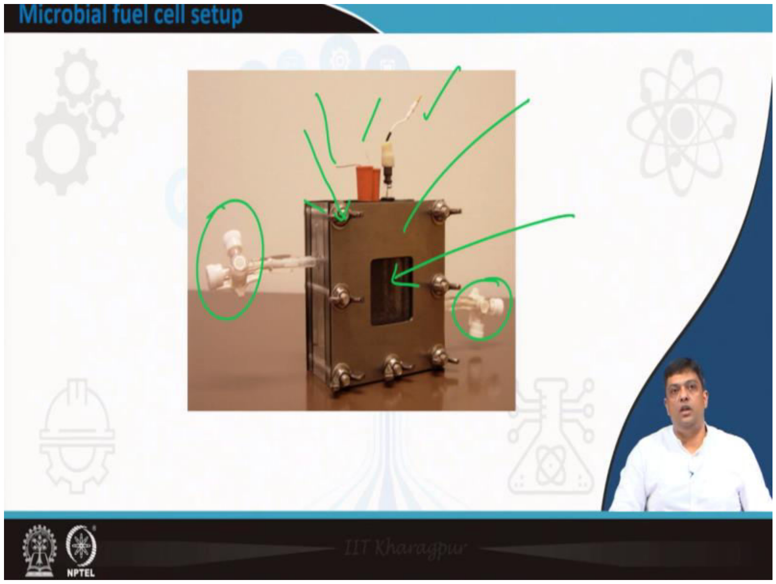


And this is what a typical fuel cell looks like, you have the outer plates, the screws, which are going across and tightening the two chambers, you have the air breathing cathodes, you have the way where you can control the flow of the influent or the effluent and then you have the reference electrodes or the nickel chromium wires for obtaining the electrons. And this is the other wire connecting the second electrode. So, this is a typical fuel cell which you can see.

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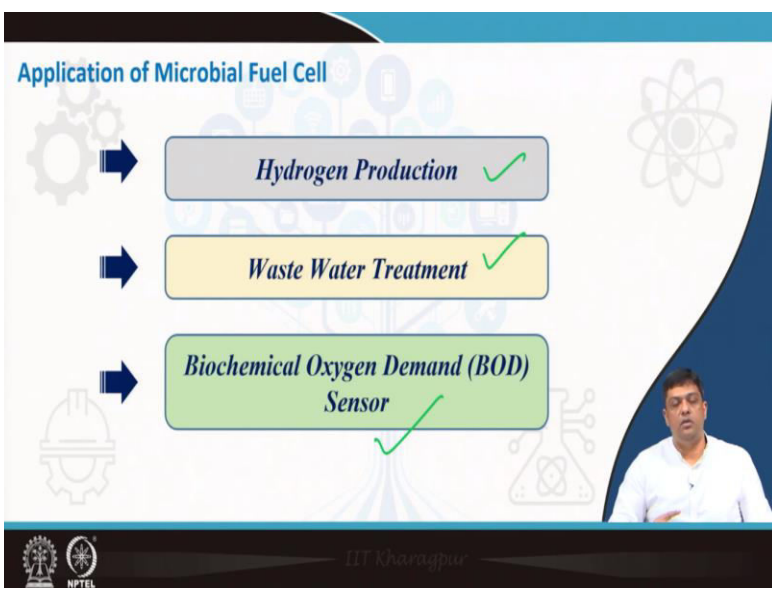

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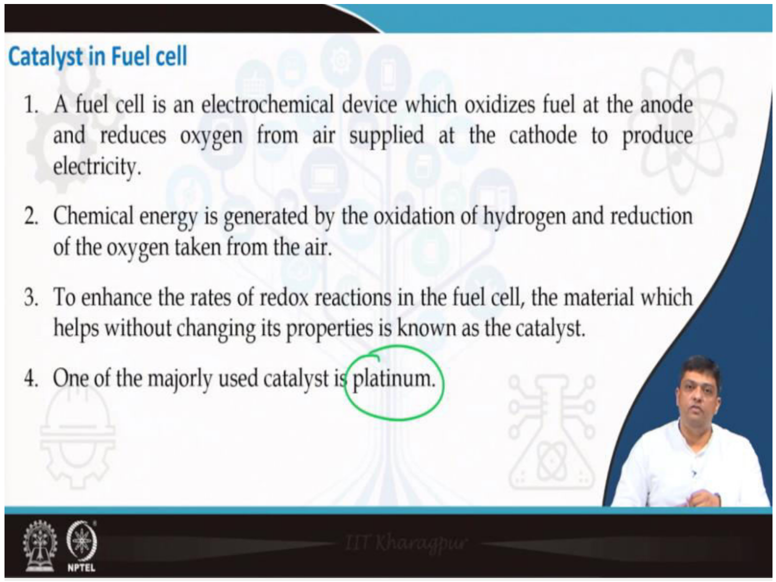


The advantage of these fuel cells are in the area of hydrogen production, waste water treatment and biochemical oxygen demand sensors. But again, the performance of these systems will depend on the use of catalysts. And till now, platinum was being extensively used till a decade or so, but now, new materials are being investigated, which have slightly less catalytic performance than platinum, but they are economically viable and they are able to deliver the characteristics required in a fuel cell.

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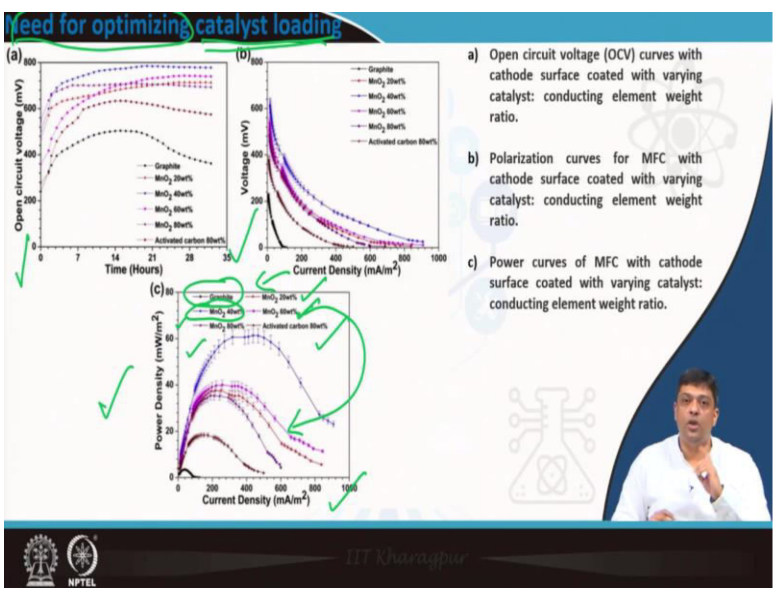

As we had seen earlier, once you have the design, once you have obtained the fuel cell, what will you do, you will obtain the polarization curves. The first measurement you will do is the open circuit voltage. The second measurement would be the polarization curves and then you will be plotting the power densities as a function of energy densities.

We have been continuously saying that use catalyst, use catalyst, but that does not mean that you can use any amount of catalyst, the loading of the catalyst on the electrode is also critical and what is the loading fraction becomes even more critical because please remember, catalysts do not initiate the reaction, they just increase the reaction rate. The initiation of the reaction is actually occurring at the electrode surface. So, if you coat the whole surface with the catalyst, then the reaction will not get initiated.

So, it is also important to optimize the catalyst loading, you can see in this case, we have used graphite as the electrode on which $MnO_2$ has been loaded as the catalyst and it is different, why because we are not used platinum, the performance is very similar, maybe slightly less in terms of power densities, but $MnO_2$ is much more cheaper than platinum. So, if you change the loading concentration, let us say 20 percent, 40 percent, 60 percent, 80 percent and then you just compare from the activated carbon.

So, you use different kinds of materials, you can clearly see the best performance is coming, when you have nearly 40 percent loading, if you go beyond that, if you go to 60 percent then the performance is actually degrading and the reason is very simple that the surface is getting coated and then the reaction is not getting initiated. So, it is easy, but you need to optimize each and every step before the device will start giving you the desired output.

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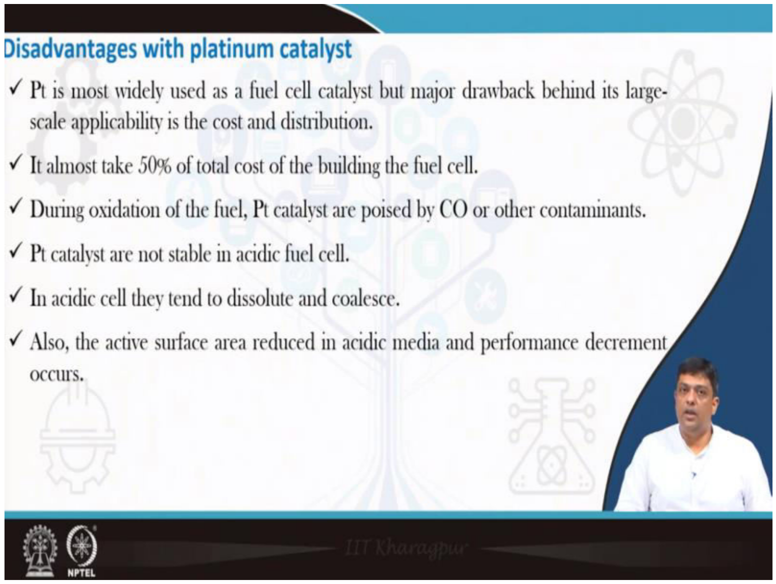


As I said, platinum is used as catalyst, but there are serious disadvantages associated with the use of platinum. The one which is mostly pointed out by everyone that is very expensive. So, you need to move to other types of catalysts to counter these limitations.

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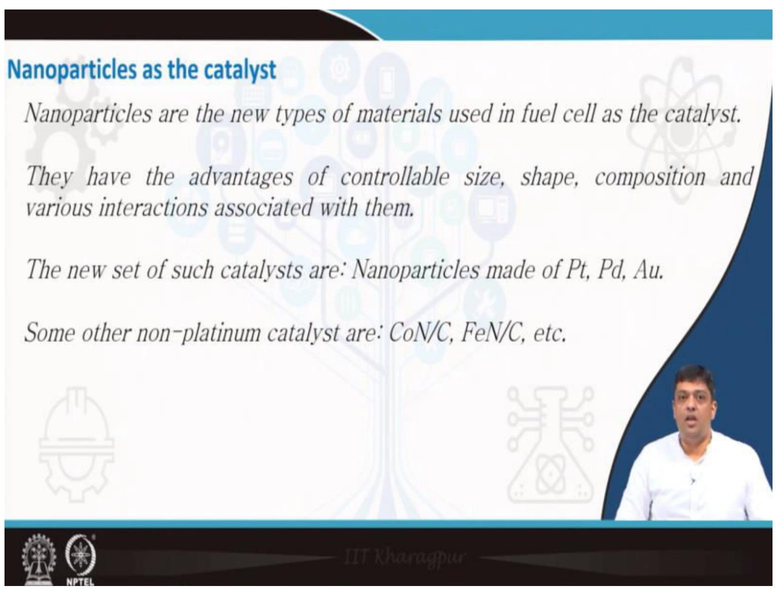


So, we have seen that platinum is mostly used, but then you need to have new materials which will replace platinum and with the advent of nanomaterials you can get large number of nanoparticles of various types of catalysts, which can actually deliver the performance that is desirable in a fuel cell.

The nanoparticles give you additional advantage that you can get them in various sizes, shapes, compositions, and you can change many of their physical and chemical properties. Therefore, with the advent of nanomaterials, the fuel cell technology is seeing a revival because the costly components can be replaced.

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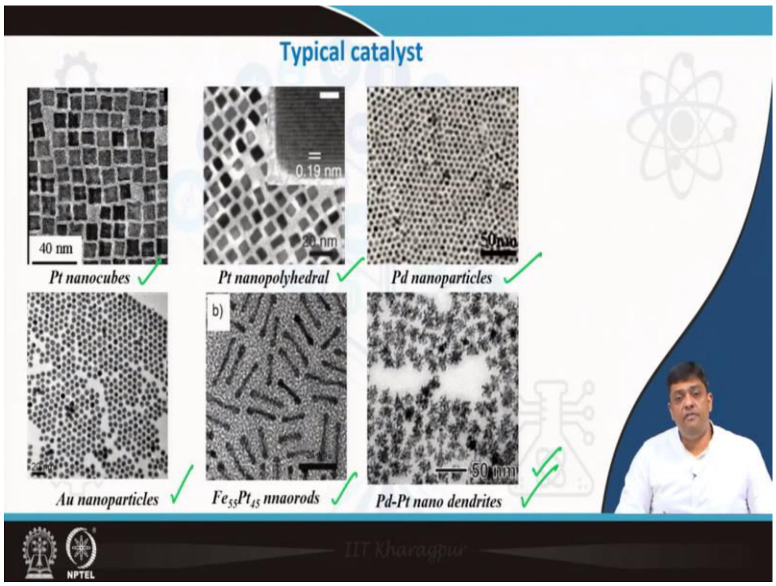


These are the typical catalysts which were initially used. Be it be platinum nanocubes, be it be platinum, nanopolyhedral type structure, be it be palladium or nanoparticles. But now, you can have gold nanoparticles, you can have a composite where you use iron with, with platinum or you can have any other kind of nano dendrites like structures made of palladium platinum composites.

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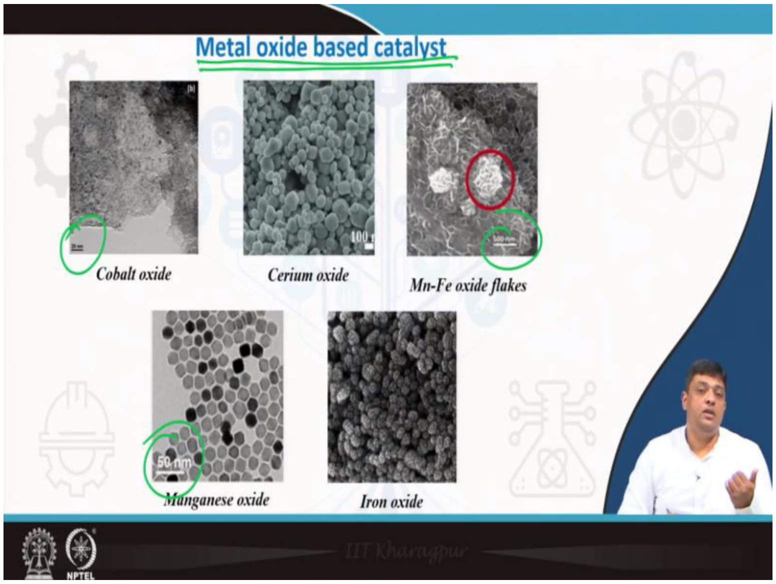


So, you can have various kinds of materials, but still in the previous case what you saw that you were using platinum. To replace platinum-based catalyst, metal oxide-based catalysts, which are in the nano scale have become quite useful. They have all the properties that you can make them in various shapes, various sizes, you can make them as porous structures and you can produce them in bulk while maintaining their economical viability. Hence, metal-based oxides are becoming quite useful in fuel cells.

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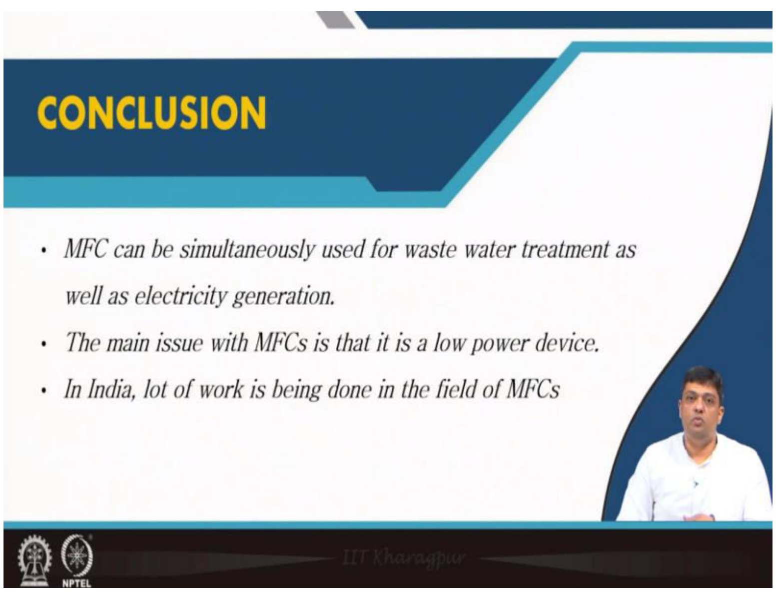

So, I hope in this final lecture of this module, I have shown to you at microbial fuel cells can be simultaneously used for wastewater treatment using microorganisms and while you are reducing the waste water, you can also get the advantage of electricity being generated by the device. As of today, the main issue which is related with MFCs is that it is a low power device. But, as more and more research is done, you will see improvement in the output from this MFCs and in India a lot of work is being done in the field of MFCs.

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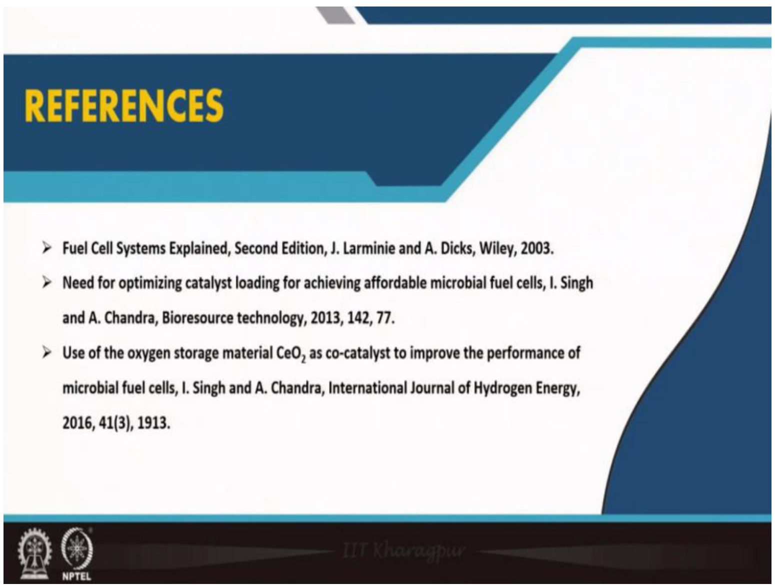


These are the major references from where the data was obtained for today's lecture. And till now, you have seen that nanomaterials will play a very important role in defining the performance of systems like lithium-ion batteries, supercapacitors, fuel cells, solar cells, or even wind turbines.

So, it is very important that we spend some time on understanding what are nanomaterials? How do they differ from bulk materials? Why do they have properties that are different from bulk materials? And if you have materials, which have different properties, then how do I fabricate those materials? And once we have fabricated those materials, how do we characterize those materials? And what are the parameters that define the characteristics of those materials?

So, the next module we will start with the discussion on nanomaterials and nanotechnology. And in the final two modules, we will talk to you about the characterization techniques used for nano material characterization as well as the device characterization devices which have been discussed in this course. Thank you very much.