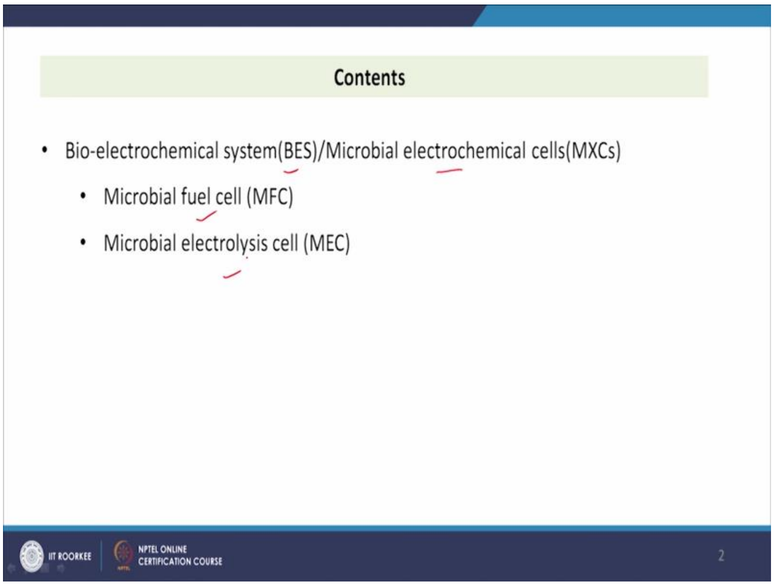
**Basic Environment Engineering and Pollution Abatement**
**Professor Prasenjit Mondal**
**Department of Chemical Engineering**
**Indian Institute of Technology, Roorkee**
**Lecture 36**
**Advanced Secondary Processes – 3**

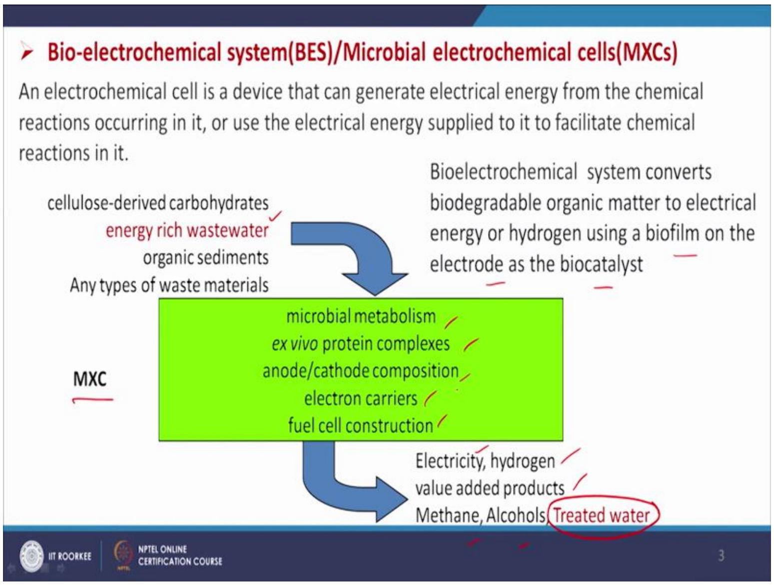
Hello everyone. Now, we will discuss on the topic Advanced Secondary Processes, Part 3. And in this class, we will discuss on bio-electrochemical system or microbial electrochemical cells.

(Refer Slide Time: 00:44)




And basically, we will be focusing on microbial fuel cells and microbial electrolysis cells.

(Refer Slide Time: 00:59)



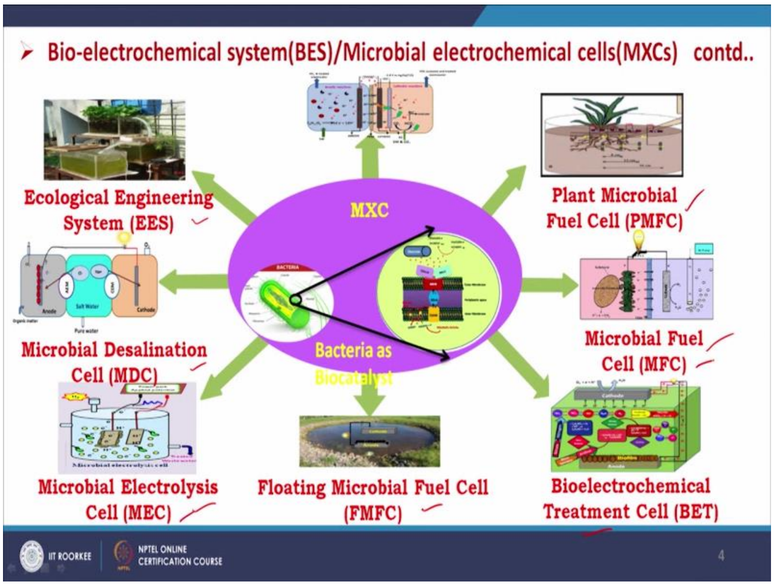
So, these bio-electrochemical systems or microbial electrochemical cells are basically a new concept or new development in the secondary treatment processes. In this case, waste water is treated and the same time some energy like electricity or hydrogen or any other valuable chemicals can also be produced.

And the term you see, that bioelectrochemical chemical systems, we have already studied electrochemical systems and we know that in electrochemical systems either the chemical energy of the system or the solution is converted to electrical energy or the vice versa. But as the bio what is added means, here the reactions will be taking place with the help of microorganisms and microorganisms will catalyze the reactions basically, for the energy component production and the degradation of the organic compound.

So, bio-electrochemical system converts biodegradable organic matter to electrical energy or hydrogen using a biofilm on the electrode as the biocatalyst. So, this is our bio-electrochemical systems. And we can summarize this whole concept like that. We are having wastewater, energy rich wastewater or any organic compounds in water solution. So, then it is going to the MXC and ultimately we will be getting electricity, hydrogen, value-added products, methane, alcohols and our main target is the treated water.

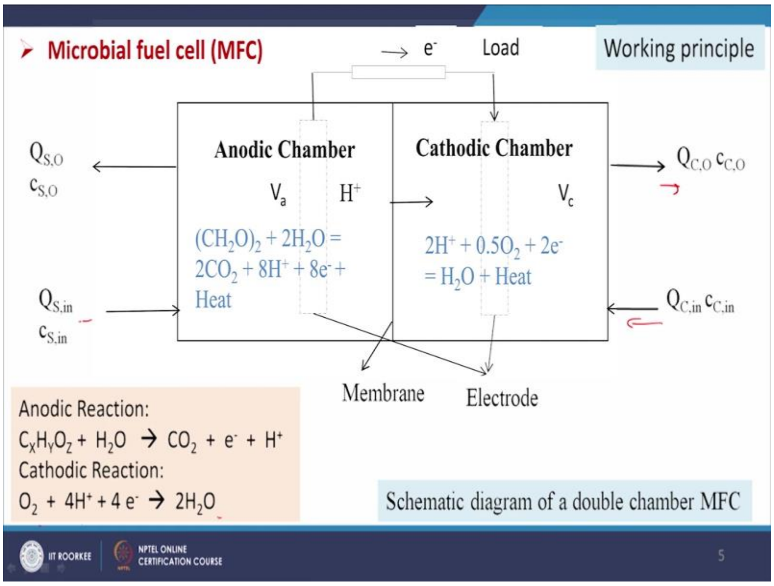
And we can use here different type of living species like say microbes, bacteria, plant, etc. and microbial metabolism ex vivo protein complexes, anode competition, electron carriers and fuel cell constructions will be influencing the performance of the process.

(Refer Slide Time: 03:18)



As I mentioned that we will be focusing on basically to MEC and MFC. So, we see here there are many other options of the bio-electrochemical systems like say plant microbial fuel cells, microbial fuel cells, bio-electrochemical treatment cells and floating microbial fuel cells, microbial electrolysis cells, microbial desalination cells and ecological engineering system. So, different systems have been developed and investigated by different researchers. And we will be focusing on the MFC and MEC.

(Refer Slide Time: 03:58)




So, first we will discuss on microbial fuel cells. So, this is the diagram which shows the working of the microbial fuel cell. So, here the organic containing wastewater is entering into the cell containing two electrodes, anode and cathode, and these two chambers are connected with this membrane.

So, this membrane allows hydrogen+ ion to transfer selectively. And here we are having some some wastewater, organic containing wastewater and microbes are also present in it. So, microbes will be working on the organic compound. For example,

$$(CH_2O)_2 + 2H_2O = 2CO_2 + 8H^+ + 8e^- + \text{Heat}$$

And this $H^+$ which is generated that will be transferred here and after a certain residence time treated water will be going out from the anodic chamber. And electron which are generated here, this electron in the bulk of the solution that will be transmitted to the surface of the anode and it will flow through an external circuit and, it will be coming to the cathodic chamber.

So, electron will move from the external circuit and come to the cathodic chamber, hydrogen plus ion will move from anodic chamber to cathodic chamber through this membrane and when it is coming here at the cathode, so, then

$2H^+ + 0.5O_2 + 2e^- = 1/2\ H_2O + Heat$

So, we need to provide some electrolytes that is catholytes, which will be having some oxygen and that oxygen will be consumed for the production of this $H_2O$ and heat and this catholyte after certain cycle it will be going out. So, during the process we are seeing that electricity is passing through an external circuit that means, we are able to get some electricity.

Electron is passing through the external circuit, so, if there is a load, we are able to get some voltage and the flow of electron, that is, the current is available in our circuit. So, that can be used for any application. Now, the anodic reactions for generalized organic compound say

$C_XH_YO_Z + H_2O \rightarrow CO_2 + e^- + H^+$

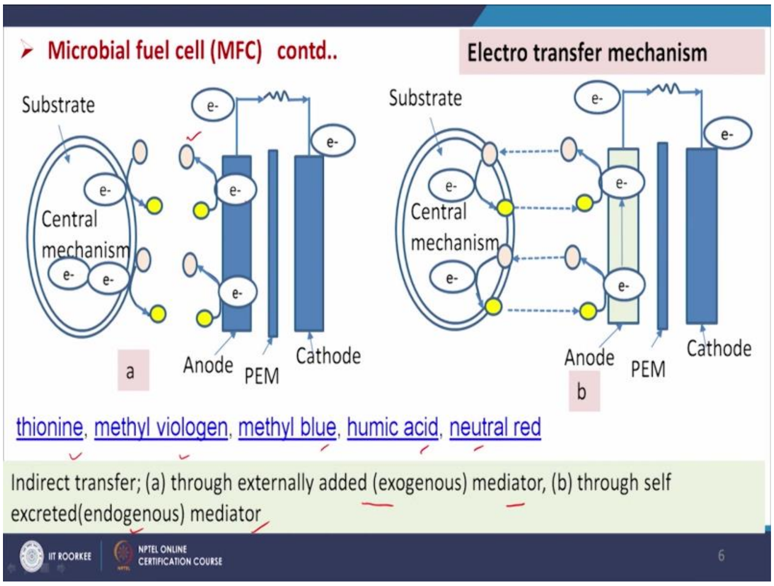
Cathodic Reaction:

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

So, this is reactions which take place in the anodic and cathodic chamber of the MFC. And in both cases, anodic chamber reactions must be catalyzed by the microorganisms. Microorganisms must be available here. In the second case that is in cathodic chamber microbes may be available or may not be available.

So, this is the overall working of the MFC. Now, we will see how the performance can be improved. And to understand that, we have to get more insight on the mechanism of the electron transfer inside it and the mechanism of hydrogen transfer to the membrane. So, that part we will be discussing now.

(Refer Slide Time: 07:52)



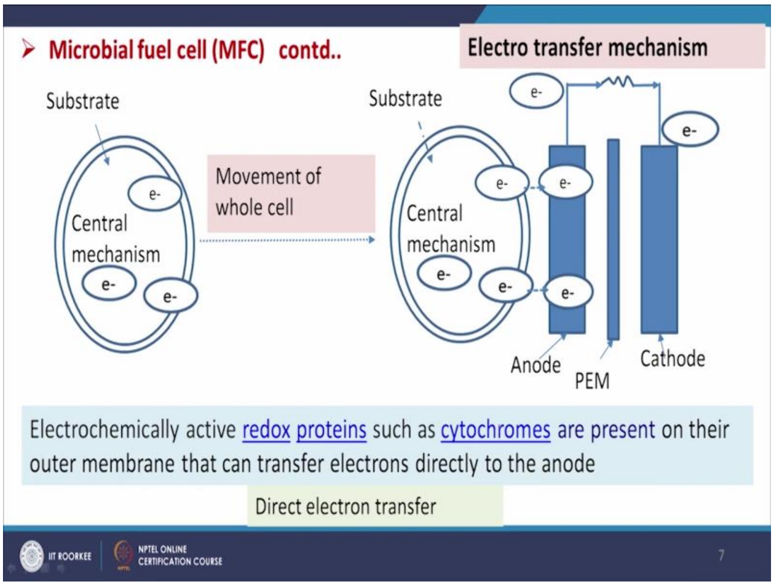

So, there are basically two types of electron transfer mechanism in the anodic chamber, one is your indirect transfer where electron which is generated by the microbial cell, which are working on the organic substance and creating electron and that electron is carried from the bulk of the solution to the surface of the electrode, that is anode, by some mediator.

So, here this is the mediator, some organic compound and some compound, those are used and that is taking electron from the cell due to the degradation of the organic compound and then electron carrying mediator is reaching here and releasing the electron and then it is again being free from the electron and again it will coming here and taking the electron and like this.

So, this way there is some material which we are adding externally, to increase the electron transfer. That is one mediator, external mediator, that is indirect transfer through externally added mediator and through self excreted endogenous mediator is also there. Here like this, if we see the mediator is generated by the cells and that is transferring the electron, releasing the electron here again it is coming back and taking the electron and going out and that way it is transferring the electron.

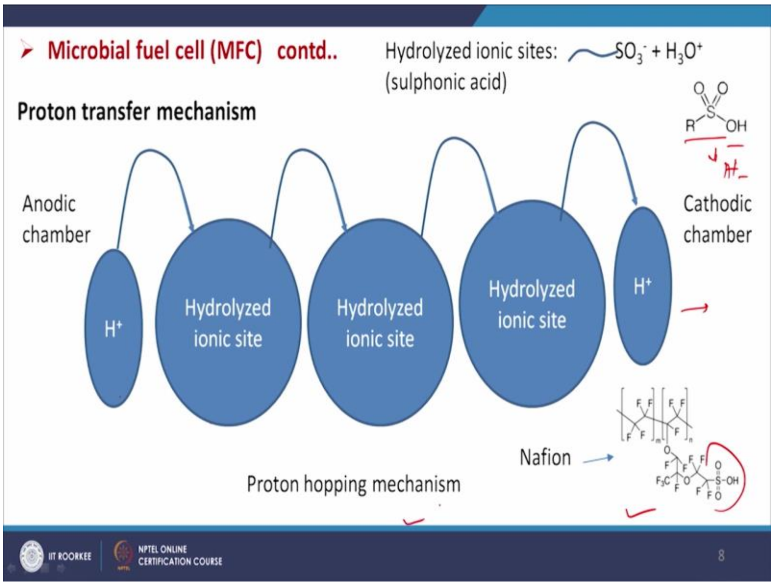
So, that is also indirectly electron is transferred to this from bulk of the solution to the anode surface. Microbes are not directly transferring the electron. But there are some other method where we will see that directly the cell is also carrying the electron from the bulk of the solution to the anode surface and leaving the electron there. Now, here we see different types of mediators which can be used externally there is thionine, methyl viologen and metal blue, humic acid, neutral red etc. So, people have used this as an external mediator

(Refer Slide Time: 10:18)




And this is the schematic diagram to represent the direct transfer. So, the electronic is generated here, the movement of the whole cell is coming here and releasing the electron to this and then electron is being transferred. So, the electro chemically active redox proteins such as cytochrome. Cytochromes are present on their outer membrane that can transfer electrons directly to the anode. So, this is the mechanism through which the electron is directly transferred from bulk of the solution to the anode surface by the itself.

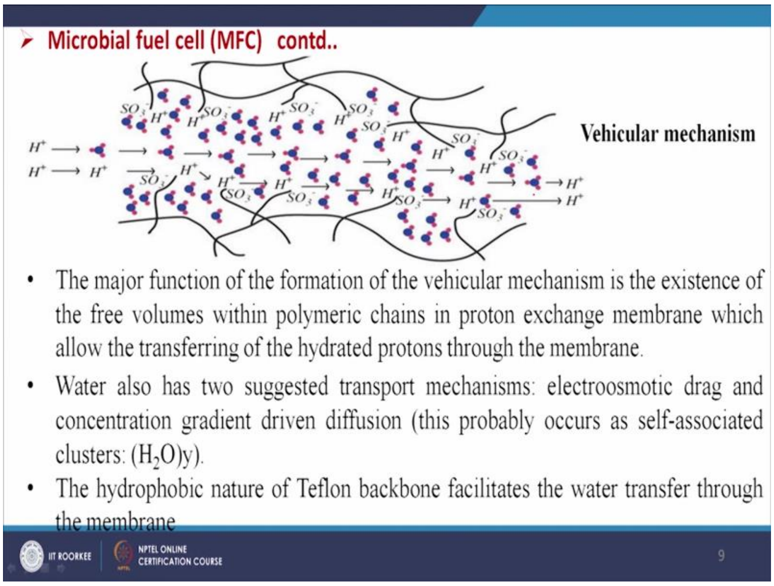
(Refer Slide Time: 10:59)



Now, we will see how the hydrogen is transferred. So, we have one membrane through which the hydrogen is transferred. So, mostly used membrane is nafion. So, this is the structure of the nafion. So, from the structure what we see that is this group is common that is R, S, O, O, OH group that is the sulphonic acid growth is very, very important and is the major part for the transfer of $H^+$ ion.

So, how would you say from the anodic chamber hydrogen is generated that is coming to the surface of this membrane and membrane hydrolyzed ionic site it is having, so, that is taking $H^+$. So, R, S, O, O, OH, so it is giving us $H^+$ + R – R, O, R, S, O, O, O – so, that minus side is taking this $H^+$ again this type of conversion will be there. So, again hydrogen will be moving from anodic to cahodic sites and then ultimately it will reach to the cathodic chamber. So, this is one way of transfer of $H^+$ ion that is called proton hopping mechanism.

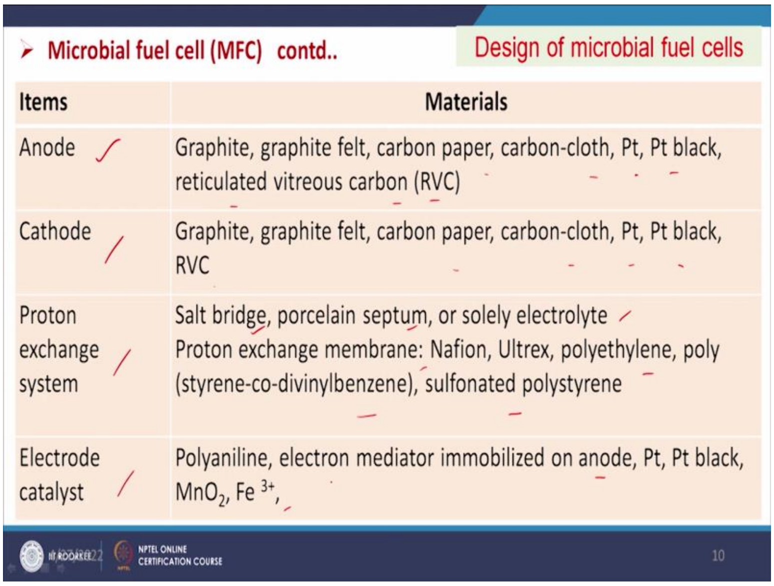
(Refer Slide Time: 12:23)




There are some other mechanism also that is vehicular mechanism. So, we have the membrane where the porosity is there, the gap is there and through which $H^+$ will be passing through. So, the major function of the formation of the vehicular mechanism is the existence of the free volumes within polymeric chains in photonics and membrane which allow the transferring of the hydrated photons through the membrane.

Water also has two suggested transfer mechanisms, electroosmotic drag and concentration gradient driven diffusion. The hydrophobic nature of the teflon backbone facilitates the water transfer through the membrane because the nafion is hydrophobic, so, water will not be attached to it. So, water with this $H^+$ that will be transferred from anode to cathode, that is the vehicular mechanism.

(Refer Slide Time: 13:22)



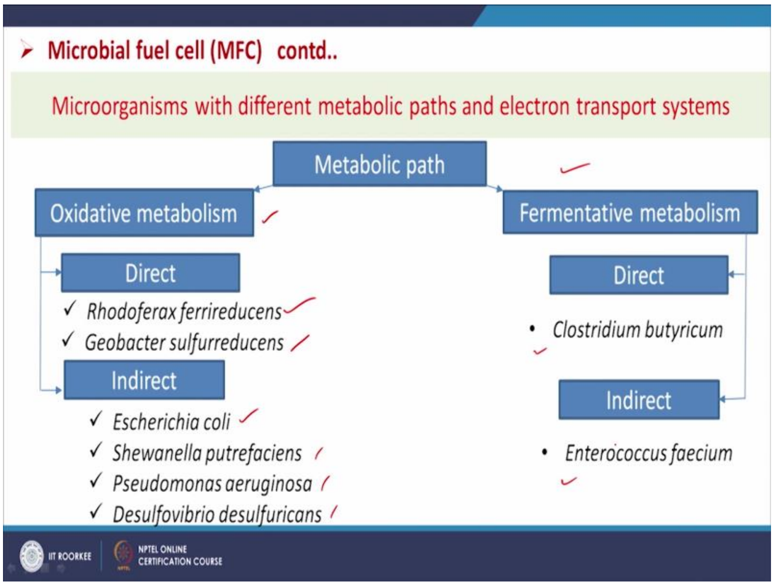

So, we are seeing here that different types of mechanisms which are responsible for the transfer of electron as well as $H^+$ ion from anodic to cathodic chamber. And more the transfer of electron and $H^+$ ion, more will be the electricity generated in the circuit, and which is desirable.

So, on the basis of this information, we can manipulate and we can optimize the performance of MEC. Now, we will see some items which are essential for the design or for the construction of microbial fuel cell like say, anode, cathode, proton exchange system and electrode catalyst.

So, different types of material have been used as anode and cathode like say graphite, graphite felt, carbon paper, carbon-cloth, platinum, platinum black, reticulated vitreous carbon, similarly, for cathode also graphite, graphite felt, carbon paper, carbon-cloth, platinum, platinum black, RVC.

And proton exchange system like very simple salt bridge and then porcelain, septum or solely electrolyte or proton exchange membrane like Nafion, Ultrex, polyethylene, poly styrene-co-divinylebenzene and sulfonated polystyrene different types of materials have been investigated. And electrode catalysts like polyaniline, electron mediator immobilized on anode, platinum, platinum black, $MnO_2$, $Fe3^+$, etc have been used as the electrode catalyst.

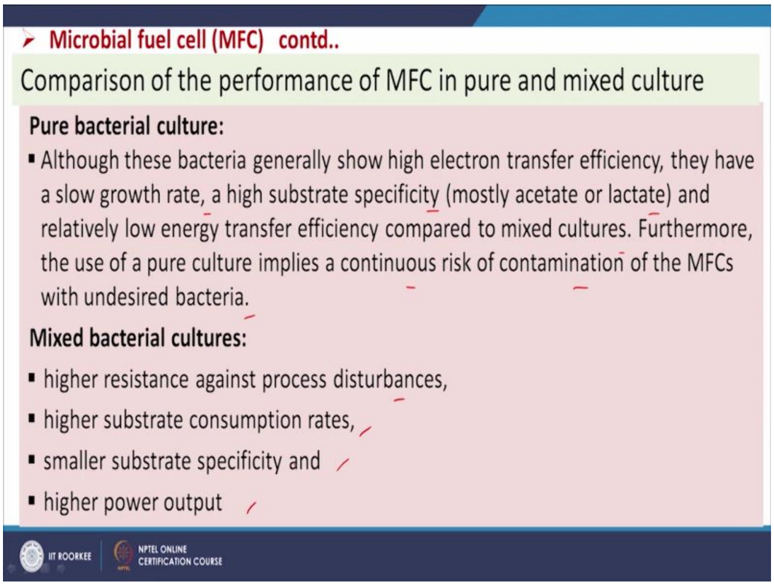
(Refer Slide Time: 15:10)




And different types of microorganisms have been investigated. And microorganisms basically follow two mechanistic part, one is oxidative mechanism and other is fermentative metabolism. And in case of oxidative, in presence of oxygen, so, the micros can directly transfer the electron from bulk of the anode to anodic chamber to anode surface, these are some example of this direct transfer.

And some indirect transfer can also be possible there are many microorganisms which cannot directly transfer. So, indirect transfer is possible different microorganisms are mentioned here. Again, for fermentative metabolism also in case of anaerobic condition, microbes can be used and direct mechanism or indirect mechanism of electron transfer can be possible. So, these are the different types of microorganisms and different paths which are followed for the generation of electron as well as the transfer.

(Refer Slide Time: 16:26)



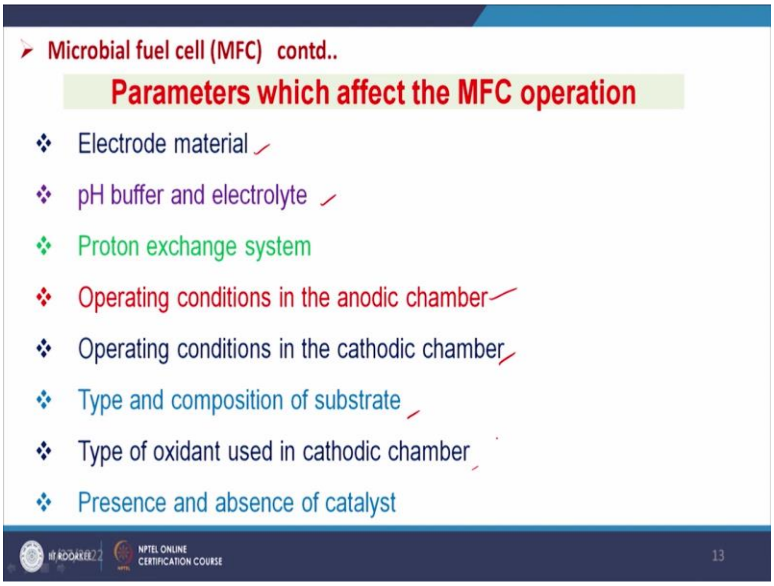

Now, we will see the comparison or performance of MFC in pure and mixed culture, because just now, we have discussed that different types of microorganisms have different capacity to work under different environment. And they have different mechanism of transfer of electron. So, if we use a pure culture, so one type of mechanism will be followed but we use a mixed culture.

So we will be having number of different microorganisms, those will be able to work under different environment and their electron mechanism is also different. So, in case of mixed culture, certainly, the system will be able to accommodate different types of socks, that means, it can be more robust than the case when only pure culture is used. But pure culture will also have some advantage. Its performance, if parameters are properly maintained, maybe better.

So, we will see here pure bacterial culture, if you use, although these bacteria generally show high electron transfer efficiency, they have a slow growth rate, a high substrate specificity, mostly acetate or lactate, and relatively low energy transfer efficiency compared to mixed cultures.

Furthermore, the use of pure culture implies a continuous risk of contamination of the MFCs with undesired bacteria. And mixed bacterial cultures give higher resistance against process disturbances, higher substrate consumption rates, smaller substrate specificity and higher power output. So, these are the advantage and disadvantage of these two types of microorganisms, if we use.

(Refer Slide Time: 18:38)




Now, we will see the parameters which affect the MFC operation. So, performance of the MFC can be influenced by different parameters. As it is a microbial system suddenly your pH buffer and electrolyte will play a role, temperature will play a role. And then electrode material will play a role because electron transfer is necessary.

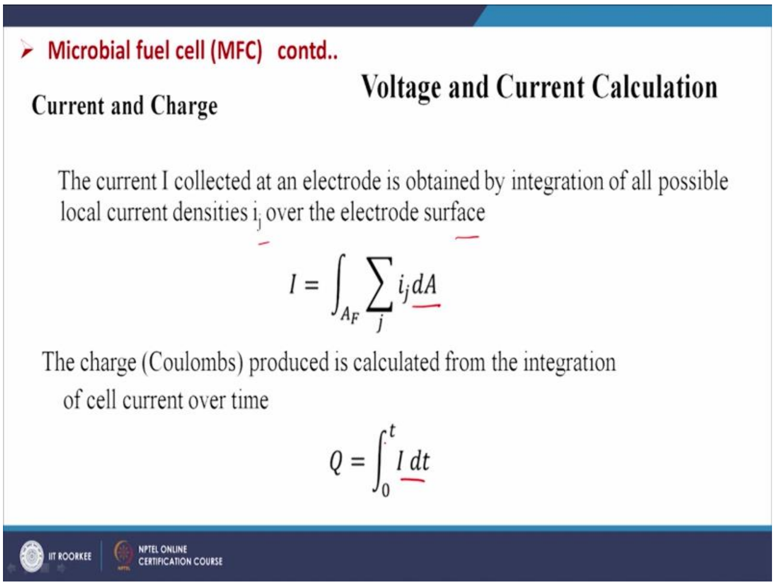
So, conductivity of the metal, if it is more, than it will be having more electron transfer capacity and operating condition in the anodic chamber that is what is the pH, what is the temperature, etc. and what is the oxygen, is available or not. So, operating condition in the cathodic chamber, as I have mentioned that, the system has to provide oxygen so that $H^+$ can combine with the electron and oxygen to convert it into $H_2O$.

So, that if we can use catholyte having more oxygen availability, the performance will be more. And then type and composition of the substrate. Again, that part is coming, whether it is biodegradable or not, if it is biodegradable, then what is the BOD-COD ratio, all those things will be dependent type and composition of substrate.

And type and oxidant used in cathodic chamber again the same case what type of oxidants we are using. There are different types of cathodes, like say air cathodes, some air some oxygen is sent, some air some chemicals, where we can get more oxygen those are also sent. So, different types of catholytes are present. So, those influences the performance of the MFC and presence and absence of catalyst.

If catalyst is present in case of cathode, so, then the electron transfer makes easier and the performance also gets improved. So, these are the different parameters which affect the MFC operation. Now, as we mentioned along with the wastewater treatment, the one another major objective of this process is to get electricity. So, how the voltage and current can be calculated, that is discussed here.

(Refer Slide Time: 20:46)




So, the current and charge in this case, we have some electrodes that is anode, so organic compound is degraded in the anodic chamber and electron is transferred from bulk of the solution to the anode surface. So, there will be some local current. So, if we sum it up, then will we get the total current. So, the current I collected at an electrode is obtained by integrating all of the possible local current densities $i_j$ over the electrode surface.

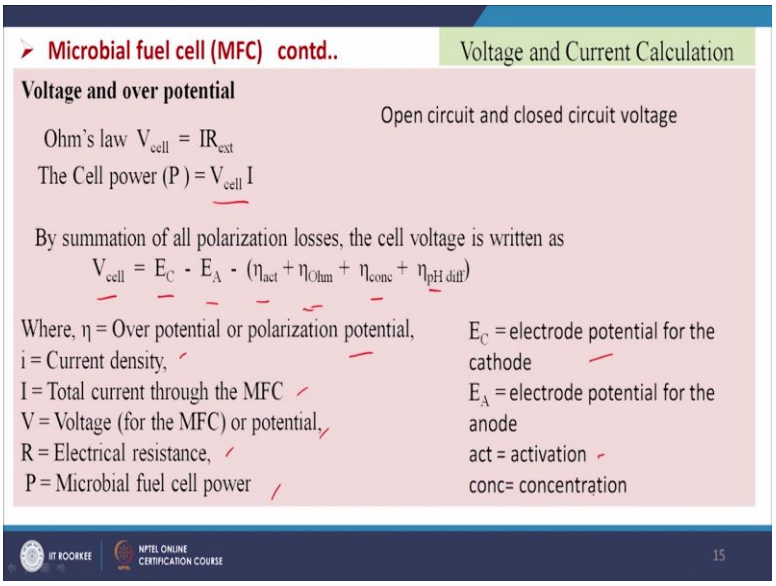
So, $I = \int_{A_F} \sum_j i_j dA$

If we get integration then we will get the total current and the charge that is certainly the current that it will be current into time, ,

$$Q = \int_0^t I\, dt$$

So, we can calculate the current and charge by that way. Then voltage and over potential, how we can calculate.

(Refer Slide Time: 21:52)




So, Ohms law tells that $V_{cell} = I^* R_{cell}$, V = I R.

And cell power = V *I,

And we know that there are open circuit and closed circuit voltage. So, when MFC is not connected with the external circuit. So, there will be some potential difference between anode and cathode, that is open circuit voltage but when you will be connecting it with some external circuit. So, continuously electron will flow. And the effective voltage, we will get, that is called a closed circuit voltage.

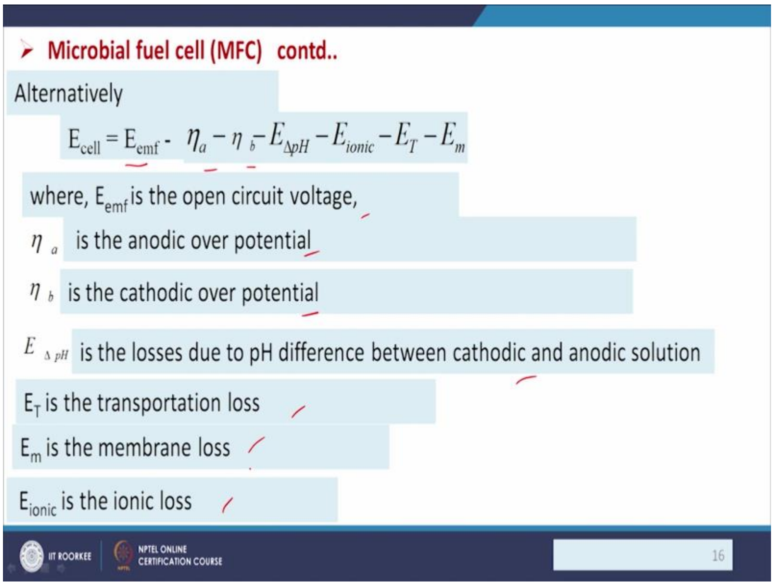
So, this open circuit voltage is always greater than the closed circuit voltage. By summation of all polarization losses, the cell voltage is written as

$$V_{cell} = E_C - E_A - (\eta_{act} + \eta_{Ohm} + \eta_{conc} + \eta_{pH\ diff})$$

So, these are the losses or over potential, we can say.

So, η is the over potential or polarization potential, i is the current density and I, total current, and V voltage or potential, R, electrical resistance, P microbial fuel cell power. So, already we have mentioned and $E_C$ is the electrode potential for the cathode, $E_A$ is the electrode potential for the anode and here act means activation losses, and concentration is concentration losses

(Refer Slide Time: 23:32)

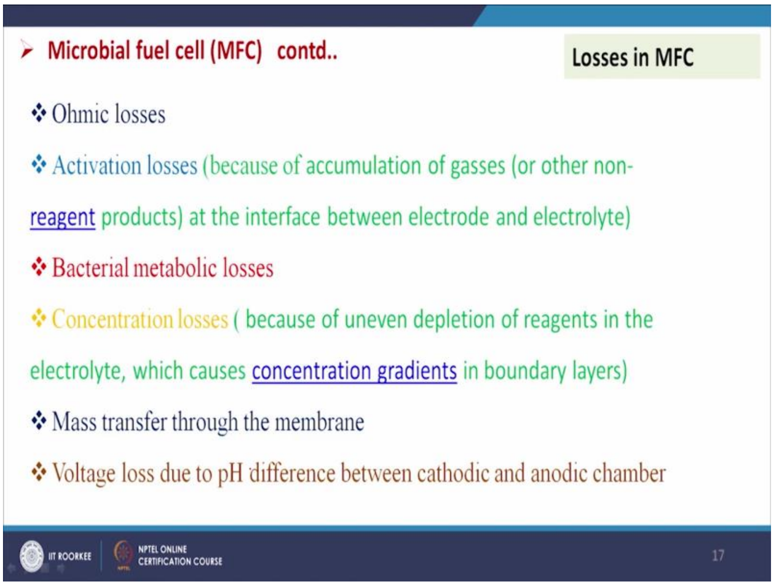



Or on the alternate way, we shall also write

$E_{cell} = E_{emf} - \eta_a - \eta_b - E_{\Delta pH} - E_{ionic} - E_T - E_m$

Where Eemf is the open circuit voltage, this is open circuit voltage minus the cathodic over potential and anodic over potential and this is the losses due to the pH difference between cathodic and anodic solution. And $E_T$ is the transportation loss and E m is the membrane loss and E ionic is the ionic loss. So, that way also we can measure the Ecell.

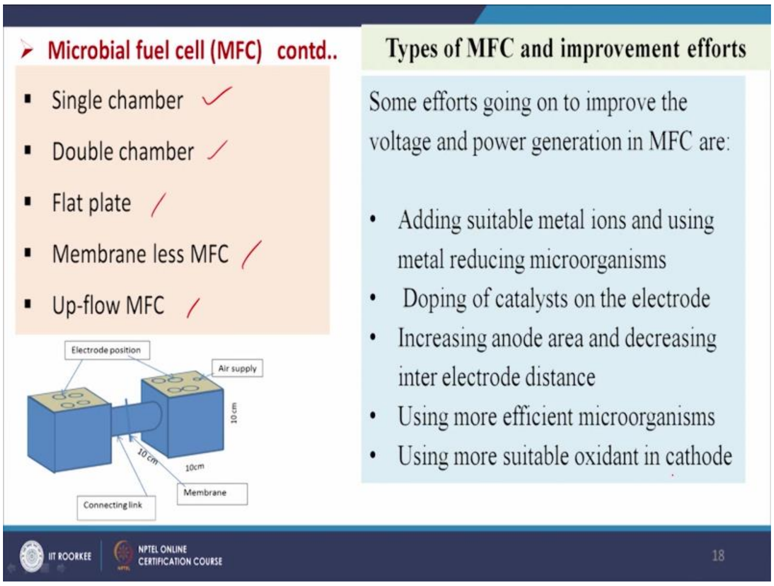
(Refer Slide Time: 24:16)




And different losses in MFC that is ohmic losses, activation losses that because of the accumulation of gases or other non reagent products at the interface between electrode and electrolytes, so, then activation losses is arised. And bacterial metabolic losses and then concentration losses because of the uneven depletion of reagents in the electrolyte, which causes concentration gradients in boundary layers.

And mass transfer through the membrane and voltage loss due to pH difference between cathodic and anodic chamber. And in this case, current and power are expressed in terms of current density and power density.

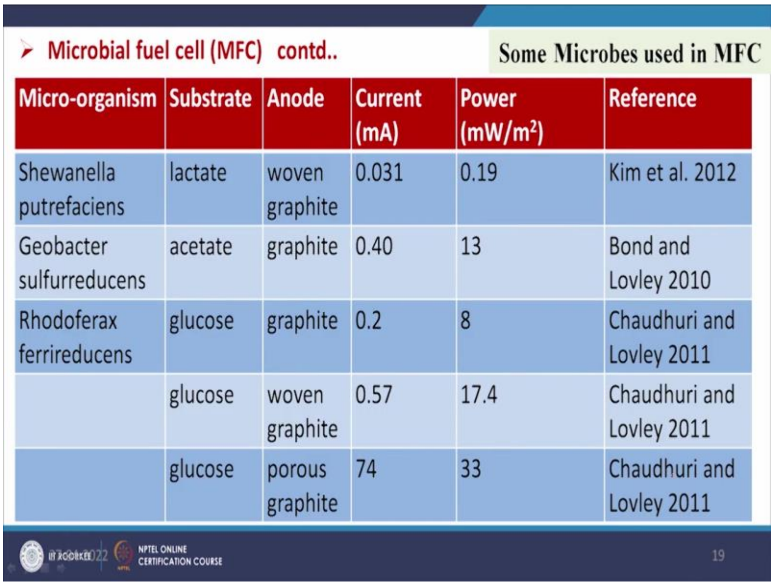
(Refer Slide Time: 25:11)




Microbial fuel cells can be of different types, it can be single chamber, maybe double chamber, maybe flat plate, may be membrane less or maybe up-flow MFC. So, this figure shows a double chamber. So, we have one membrane or other arrangement like salt bridge to separate anodic and cathodic solution.

And some efforts going on to improve the voltage and power generation in MFC also and those are adding suitable metal ions and using metal reducing microorganisms. Doping of catalyst on the electrode, increasing anode area and decreasing inter electrode distance, using more efficient microorganisms, using more suitable oxidant in cathode.

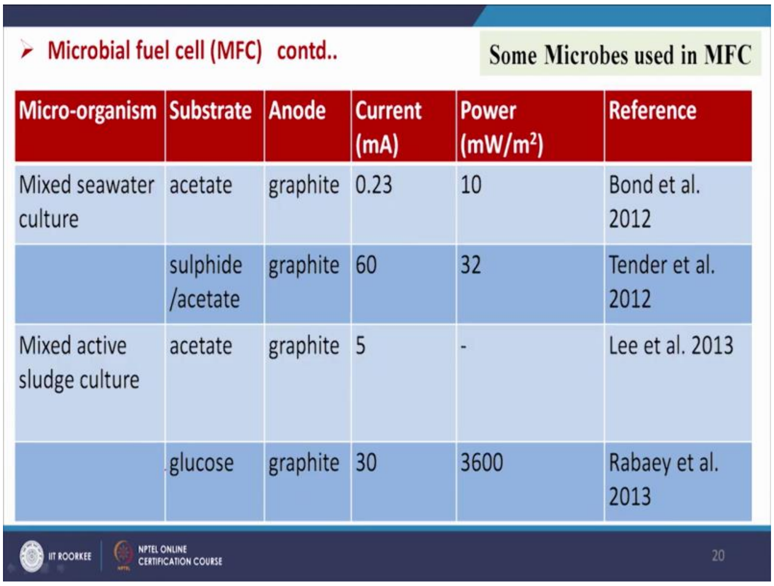
(Refer Slide Time: 26:01)




| Micro-organism | Substrate | Anode | Current (mA) | Power ($mW/m^2$) | Reference |
|---|---|---|---|---|---|
| Shewanella putrefaciens | lactate | woven graphite | 0.031 | 0.19 | Kim et al. 2012 |
| Geobacter sulfurreducens | acetate | graphite | 0.40 | 13 | Bond and Lovley 2010 |
| Rhodoferax ferrireducens | glucose | graphite | 0.2 | 8 | Chaudhuri and Lovley 2011 |
| | glucose | woven graphite | 0.57 | 17.4 | Chaudhuri and Lovley 2011 |
| | glucose | porous graphite | 74 | 33 | Chaudhuri and Lovley 2011 |

And these are some example of the use of microbes in MFC and the electricity generation. So, here we see different types of fuel compounds have been used and their current and power generation have been determined.

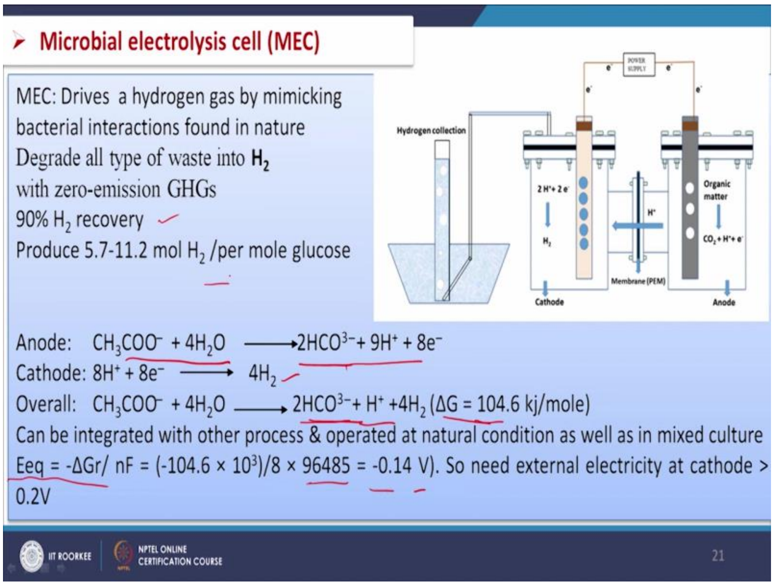
(Refer Slide Time: 26:19)




| Micro-organism | Substrate | Anode | Current (mA) | Power ($mW/m^2$) | Reference |
|---|---|---|---|---|---|
| Mixed seawater culture | acetate | graphite | 0.23 | 10 | Bond et al. 2012 |
| | sulphide /acetate | graphite | 60 | 32 | Tender et al. 2012 |
| Mixed active sludge culture | acetate | graphite | 5 | - | Lee et al. 2013 |
| | glucose | graphite | 30 | 3600 | Rabaey et al. 2013 |

Mixed wastewater have been also been used and their power generation has also been determined.

(Refer Slide Time: 26:27)




Now, we will see the MEC, microbial electrolysis cell. So here, when MEC is developed, then we see that

$H^+ + O_2 + \text{electron} \rightarrow H_2O$

That reaction can be changed if we apply some external voltage at the cathode. So, in this case for example, say if we have acetate,

Anode: $CH_3COO^- + 4H_2O \rightarrow 2HCO^{3-} + 9H^+ + 8e^-$

Cathode: $8H^+ + 8e^- \rightarrow 4H_2$

Overall: $CH_3COO^- + 4H_2O \rightarrow 2HCO^{3-} + H^+ + 4H_2$ ($\Delta G = 104.6$ kj/mole)

And this can be integrated with other procession operated natural conditions as well as in mixed culture.

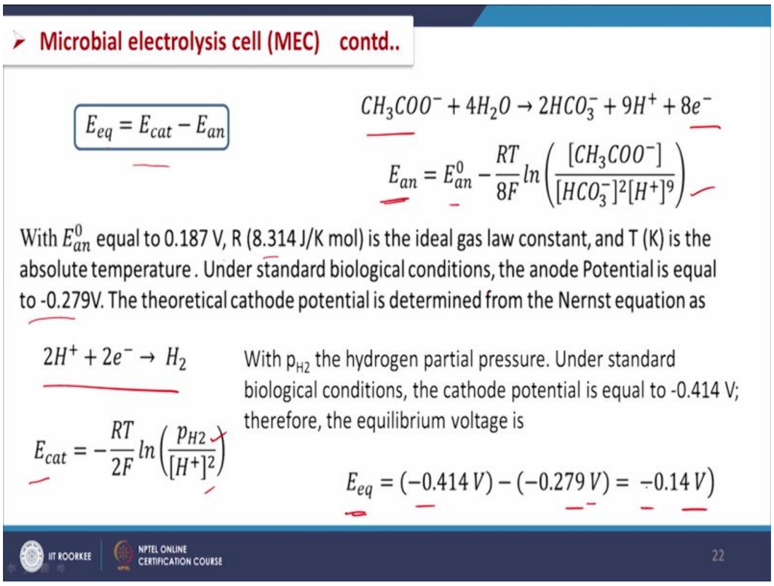
And then equivalent current,

$E_{eq} = -\Delta Gr/nF = (-104.6 \times 10^3)/8 \times 96485 = -0.14$ V).

So, in this case Gr is 104.6 and n is here 8 and F is that Faraday's constant value. So, this, by putting these value we are getting -0.14 volt. So, this amount of voltage is needed at the cathode for performing this reaction, so, which reaction was taking place in MFC.

We can stop it, and that reaction can be converted to this mode by the application of this external voltage. MEC this device is a hydrogen gas by mimicking bacterial interactions found in nature. It degrades all type of waste into hydrogen with zero emission and 90 % hydrogen recovery, and it can, 5.7 to 11.2-mole hydrogen per mole of glucose.

(Refer Slide Time: 28:50)




Now, equivalent voltage,

$$E_{eq} = E_{cat} - E_{an}$$

And in case of anode what is the reaction, this is a reaction.

$$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^-$$

$$E_{an} = E^0_{an} - \frac{RT}{8F} \ln\left(\frac{[CH_3COO^-]}{[HCO_3^-]^2[H^+]^9}\right)$$

So, this is as per the expression, this will be our anodic voltage.

And in the cathodic voltage, this is the reaction

$$2H^+ + 2e^- \rightarrow H_2$$

$$E_{cat} = -\frac{RT}{2F} \ln\left(\frac{p_{H_2}}{[H^+]^2}\right)$$

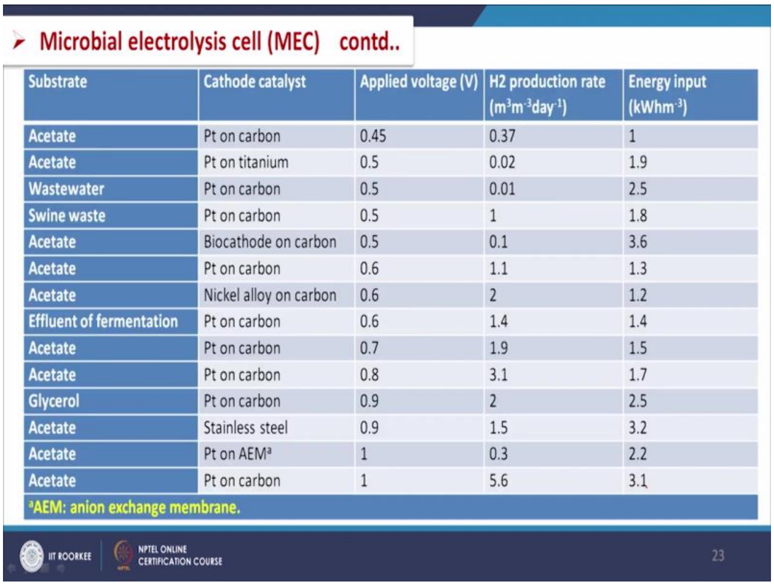
So, the equivalent voltage will be

$$E_{eq} = (-0.414\ V) - (-0.279\ V) = -0.14\ V)$$

Because here, the $E_0$ anode that is equal to 0.187 volt and R equal to 8.314 joule per kilo mole is the ideal gas law constant. And T is the absolute temperature.

So, under standard biological conditions, the anode potential is equal to 0.279 volt. So, this is given, so, by this minus this it is giving minus 0.14 volt. That means, this voltage is essential at cathode. So, you have to add some external voltage source minimum 0.14 volts, as per this expression, but we have to provide some more.

(Refer Slide Time: 30:53)



Microbial electrolysis cell (MEC) contd..

| Substrate | Cathode catalyst | Applied voltage (V) | H2 production rate ($m^3 m^{-3} day^{-1}$) | Energy input ($kWhm^{-3}$) |
|---|---|---|---|---|
| Acetate | Pt on carbon | 0.45 | 0.37 | 1 |
| Acetate | Pt on titanium | 0.5 | 0.02 | 1.9 |
| Wastewater | Pt on carbon | 0.5 | 0.01 | 2.5 |
| Swine waste | Pt on carbon | 0.5 | 1 | 1.8 |
| Acetate | Biocathode on carbon | 0.5 | 0.1 | 3.6 |
| Acetate | Pt on carbon | 0.6 | 1.1 | 1.3 |
| Acetate | Nickel alloy on carbon | 0.6 | 2 | 1.2 |
| Effluent of fermentation | Pt on carbon | 0.6 | 1.4 | 1.4 |
| Acetate | Pt on carbon | 0.7 | 1.9 | 1.5 |
| Acetate | Pt on carbon | 0.8 | 3.1 | 1.7 |
| Glycerol | Pt on carbon | 0.9 | 2 | 2.5 |
| Acetate | Stainless steel | 0.9 | 1.5 | 3.2 |
| Acetate | Pt on AEM[a] | 1 | 0.3 | 2.2 |
| Acetate | Pt on carbon | 1 | 5.6 | 3.1 |

[a]AEM: anion exchange membrane.



So, that is why minimum 0.2 is provided and we increase the external voltage, initially the hydrogen production rate increases. In some cases, we may get some optimum value of this external voltage for getting maximum hydrogen production. And good amount of research is going on, people are working on this area.

Like say different types of cathode catalysts have been used and different applied voltage have been used, different hydrogen production rates have been achieved and energy input is also varied. So, these methods are basically used for the production of energy component through the treatment of wastewater. So, it is considered as advanced stage. And as in this process microbes are being used. So, these are under the secondary treatment category.

So, up to this in this class. Thank you very much for your patience.