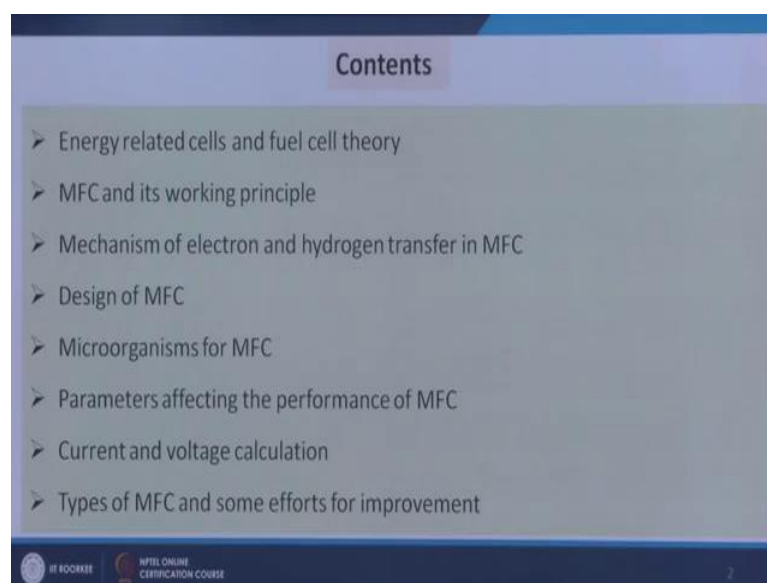


Waste to energy conversion
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Lecture – 29
Introduction to Microbial fuel cells

Good morning. Now we will start discussing on a new module Introduction to Microbial Fuel Cells. As you know microbial fuel cells are device which produces electricity from the chemical energy stored in organic molecules present in the waste water or any aqua solution by the microbial activity. This is a new relatively new technology and emerging gradually, the mechanism of MFC is similar to that of fuel cells, only difference is the microbes' acts as catalyst and organic load present in the waste water or any aqua solution acts as the fuel.

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So, in this module we will discuss on energy related sales and fuel cell theory, then microbial fuel cells and it is working principle then mechanism of electron and hydrogen transfer in MFC, then design of MFC microorganisms for MFC parameters affecting the performance of MFC, and current and voltage calculation, and finally types of MFC and some efforts for its improvement.

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Different types of cells related to energy

Galvanic cell : It converts chemical energy to electrical energy.

Electrolytic cell : It converts electrical energy into **chemical free energy**.

Batteries : Devices that carry out these conversions. Conventionally these supply electrical energy from the chemical reactants stored within them.

Fuel Cell: An electrochemical device in which the free energy of a chemical reaction is converted to electrical energy. The reactants are supplied from an external source as they are consumed. No combustion and no NO_x emissions.

Microbial fuel cells: A fuel cell in which chemical reaction is replaced by microbial reaction and the organic load of waste water is used as fuel.

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Now, let us the energy related cells. We have heard about galvanic cells we have heard about electrolytic cell. We know batteries we know fuel cells and we also know microbial fuel cells. So, the galvanic cell, converts chemical energy to electrical energy whereas, electrolytic cell converts electrical energy to chemical energy. And battery is a device which helps to convert this type of energy from chemical to electrical and electrical to chemicals, during recharging the electrical to chemicals energy converts.

And fuel cells are an electrical device in which free energy of a chemical reaction is converted to electrical energy. The reactants are supplied from an external source as they are consumed in this case no combustion, it is there and no nox is produced. So, in microbial fuel cells a fuel cell in which chemical reaction is replaced by microbial reaction.

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Fuel cell theory

- A fuel cell consists anodic and cathodic chamber. Separated by Electrolyte which allow the flow of proton and restrict the flow of electron.
- Hydrogen and Oxygen are fed into the cell.
- Catalyst at anode causes hydrogen atoms to give up electrons leaving positively charged protons.
- Oxygen ions at cathode side attract the protons.
- Protons pass through electrolyte membrane.
- Electrons are redirected to cathode through external circuit, which makes current.

Reactions:

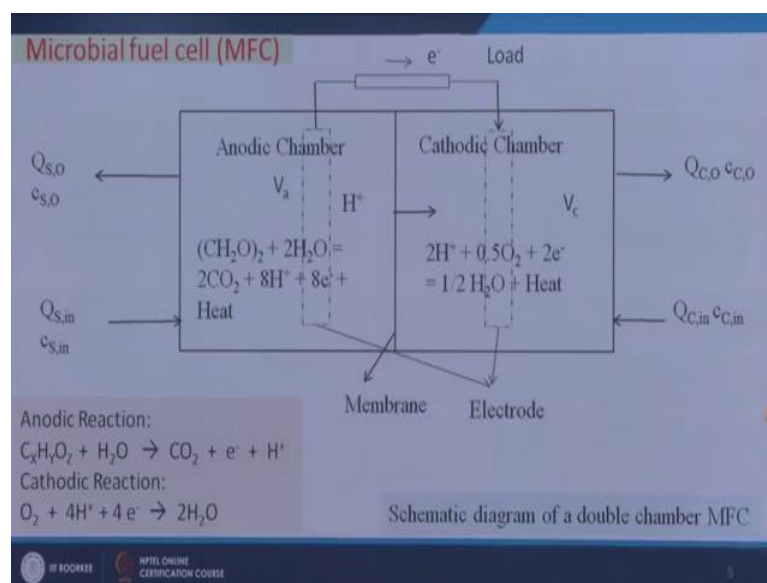
Cathode: $\text{H}_2 \xrightarrow{\text{Catalyst}} \text{H}^+ + \text{e}^-$

Anode: $\text{O}_2 + \text{H}^+ + \text{e}^- \xrightarrow{\text{Catalyst}} \text{H}_2\text{O}$

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So, now we will discuss the theory of a fuel cell with respect to hydrogen fuel cell. If we consider hydrogen fuel cell, then in this case a fuel comes in the anode. So, in the anodic chamber the fuel gets entry where the fuel that is hydrogen is converted to H plus and E minus in presence of catalyst as shown here these are the catalyst in the anodic cell. So, then the electron which is produced here is transported from this anodic to cathodic chamber through the external circuit where we can get electricity. And this H plus which is produced here in the anodic chamber moves towards the cathodic chamber through some membrane or electrolyte barrier. So, this is the mechanism of the fuel cell. In this case no combustion of the fuel is required no nox is formed. Now if we consider microbial fuel cell.

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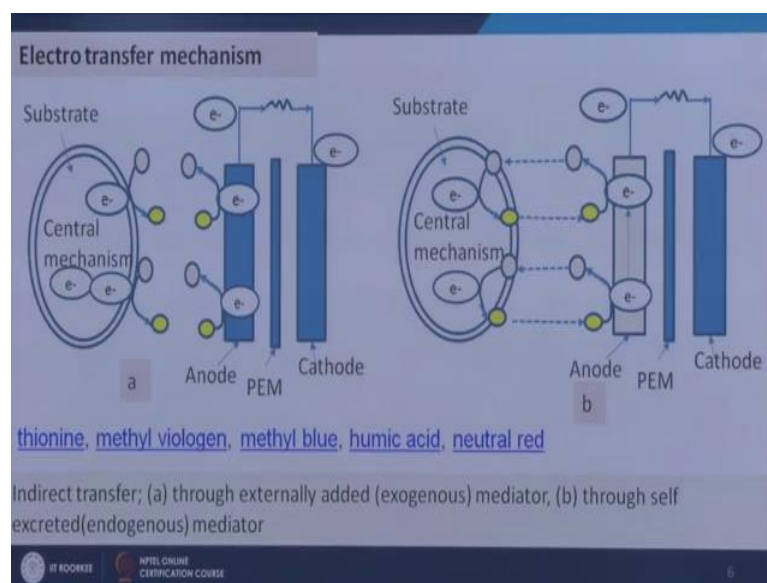


Then the reaction will be similar. Only the microbes will help as catalyst and the organic load present in the waste water or water stream will be used as fuel.

So, one example is given here say this is a double chamber. So, this is the membrane which is separating anodic and cathodic chamber just like fuel cell if we think here the same. And here the reaction is going on these are the reactions. So, electron and H plus is formed. So, in the anodic reactions and cathodic reactions also we see oxygen we supply here in fuel cell then electron comes that electrons oxygen and H plus in presence of catalyst water is formed. The similar mechanism here electron is coming from the external circuit and hydrogen is passing through this and then reaction is going on and we are getting H₂O water and heat.

But in this case the catalyst is there, but here the catalyst may be microbes or may be some other agent, but here microorganisms are massed. In the anodic chamber microorganism are massed. So, this is the mechanism of microbial fuel cell which is very similar to that of fuel cell. Now the question comes how the electron and hydrogen is transferred from anodic to cathodic chamber. Because more the electronic transfer more we will get the electricity. So, our interest is to get more electron transfer. So, if we understand what is the mechanism, we can understand the resistance available and we can take proper action to reduce the resistance of electron transfer.

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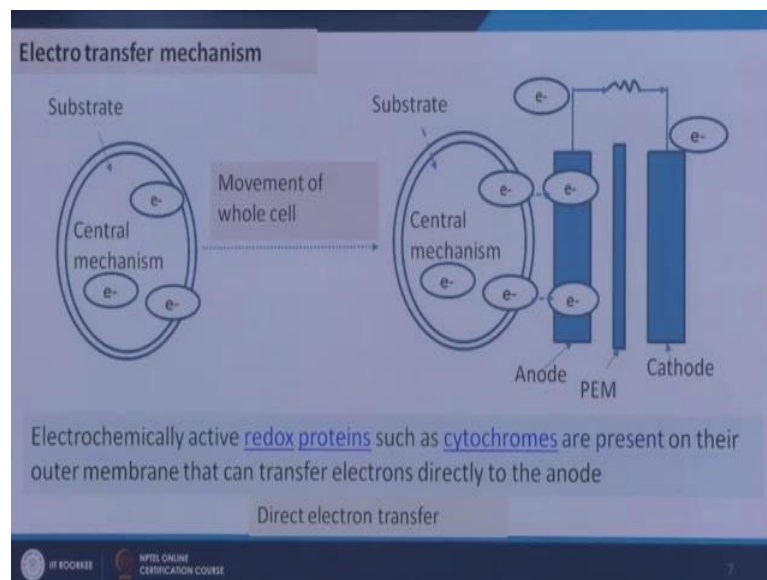
So, here we will discuss the electron transfer mechanism basically there are 2 types of mechanism that is indirect electron transfer and direct electron transfer.

What happens in case of microbial fuel cell, we are considering that organic compounds are converted to electron and H^+ and CO_2 gas. So, that would that reaction will take place there is microbial reaction and will take place in the bulk of the solution that is in this anodic chamber. And that electron has to be transferred to this electrode first, then electrode to cathode anode to cathode through external circuit. So, this is metallic or any this transfer is fast relatively with respect to the transfer of electron from bulk to this; so anode surface bulk to anode surface that is relatively slower step. So, we will be concentrating here how the electron is transferred from bulk of the solution to the anode surface.

So, there are 2 mechanisms one is direct mechanism and another is indirect mechanism. So, this is indirect mechanism. That means, microorganism does not have any capacity to transfer electron which is generated during the microbial activity to the anode surface. So, some external agents are added, or sometimes microorganisms itself creates some material that helps to transfer the electron. So, this is called indirect transfer and this indirect transfer basically can be of type 1 and type b. So, type a is externally added mediator. So, mediators are needed which are added externally takes the electron from the surface of this cell and then it moves towards the anode release the electron and again

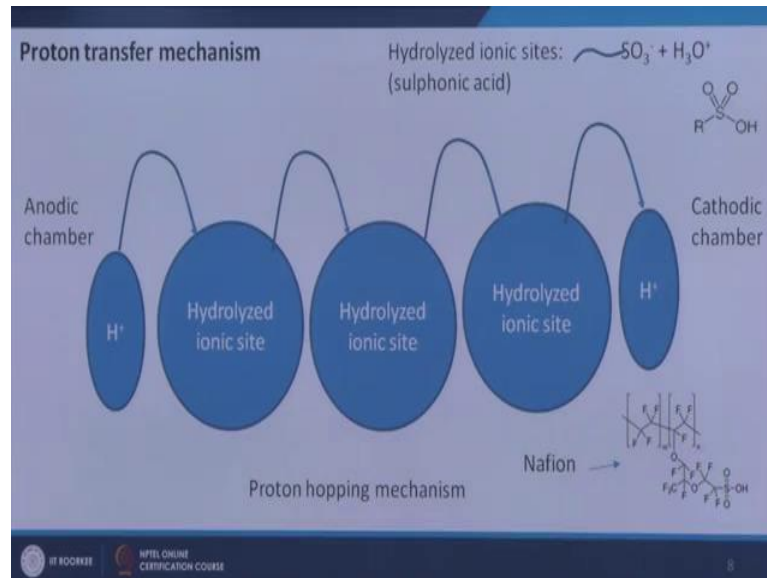
it is oxidized. So, this is the case oxidation and reductions cycle is going on, by the external agent, but here this is indirect route, but this oxidizing and redoxing agent oxidation reduction taking place this agent is generated by the microbes, itself due to it is excretion. So, through self excreted mediator that is called.

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But, in other case for direct mechanism the electron is produced the microbial cells and that is being coming at the surface of it and the microbes itself is moving towards the electrode that is anode and transferring electron. So, these transfers take place through cytochromes or some redox proteins. So, this is the direct transfer of electron.

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Next, we will see how the hydrogen is transferred from anodic to cathodic chamber. So, here say this is anodic chamber we have some layer here.

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$$E_{\text{cell}} = E_{\text{anode}} - \eta_a - \eta_c - E_{\text{OH}} - E_T - E_M - E_{\text{conc}}$$

So, if this is our anodic chambers there is some layer, or say membrane we can say. So, this is anodic chamber and this is cathodic chamber. So, hydrogen is moving in this direction hydrogen is moving. So, in this say membrane is made off some compound. So, basically mostly used membrane for hydrogen transfer is nafion and it is our nafion is having the structure of the nafion.

So, here we are seeing that SO_3H group is present with some a long chain. So, this chain is SO_3^- and H^+ is produced due to hydroxylation of this sulphonic acid. So, this sulphonic acid group is hydrolyzed to SO_3^- and H^+ . So, this one hydrolyzed ionic side we are considering then SO_3^- this is converted to SO_3^- plus H^+ . So, H^+ is moving towards this, and then H^+ is added to this part SO_3^- part. So, then H^+ is moving in this directions that is from anodic chamber to cathodic chamber and when it reaches to this end of this end of this media or say membrane then the H^+ goes to the cathodic chamber and H_2O is formed.

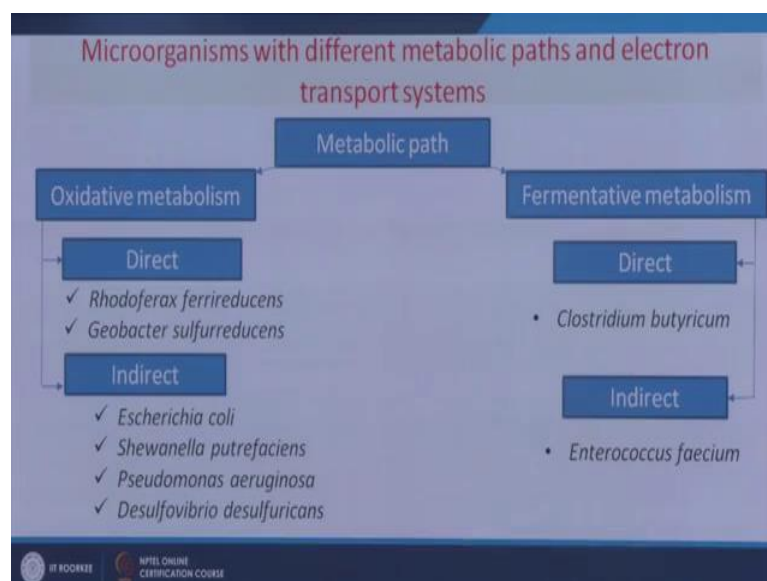
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Design of microbial fuel cells	
Items	Materials
Anode	Graphite, graphite felt, carbon paper, carbon-cloth, Pt, Pt black, reticulated vitreous carbon (RVC)
Cathode	Graphite, graphite felt, carbon paper, carbon-cloth, Pt, Pt black, RVC
Proton exchange system	Salt bridge, porcelain septum, or solely electrolyte Proton exchange membrane: Nafion, Ultrex, polyethylene, poly(styrene-co-divinylbenzene), sulfonated polystyrene
Electrode catalyst	Polyaniline, electron mediator immobilized on anode, Pt, Pt black, MnO_2 , Fe^{3+} ,

So, this is the mechanism of hydrogen transfer through the wooden exchange membrane. Now these are different parts which are required for the working of MFC. So, those are anode cathode photon exchange system and electrode catalyst. So, electrode catalyst may not be always applicable, but these 3 are always required. So, anode and cathode may be of the same type of material. So, for graphite felt carbon paper etceteras different types of materials has been used as mentioned in this table photon exchange systems may be a membrane or may be salt bridge or may be some electrolyte.

So, different types of systems have been used. And then electrode catalyst this is not used everywhere, but this helps to transfer the electron and electron mediator immobilized on anode. So, these are the electrode catalyst which have been reported in literature are mentioned here.

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Now let us see the microorganisms which are responsible for this degradation of the organic compounds and they are metabolic routes and the route through which the electron is transferred. So, metabolic path may be oxidative or may be fermentative. So, in presence of oxygen in absence of oxygen the reactions take place, if we see the dual chamber microbial fuel cell. So, here oxygen we are supplying. So, the catalyst if we used or microorganisms, if we use here that will be working in oxygen environment, but here the microorganisms are working in anoxic environment.

So, that is why two types of metabolisms are there for the working of microbial fuel cells. So, 2 types of microbes. So, examples of these microorganisms which are responsible for direct electron transfer and indirect electron transfer are provided in this slide.

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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
Rhodospirillum rubrum	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

Now, we will see some microorganisms which have been used for the production of electricity from organic load present in water and waste water; so Shewanella, Geobacter, Rhodospirillum. So, these are used by these authors and these are the output or in terms of power generation and different types of substrate have been used and different anode materials have been used.

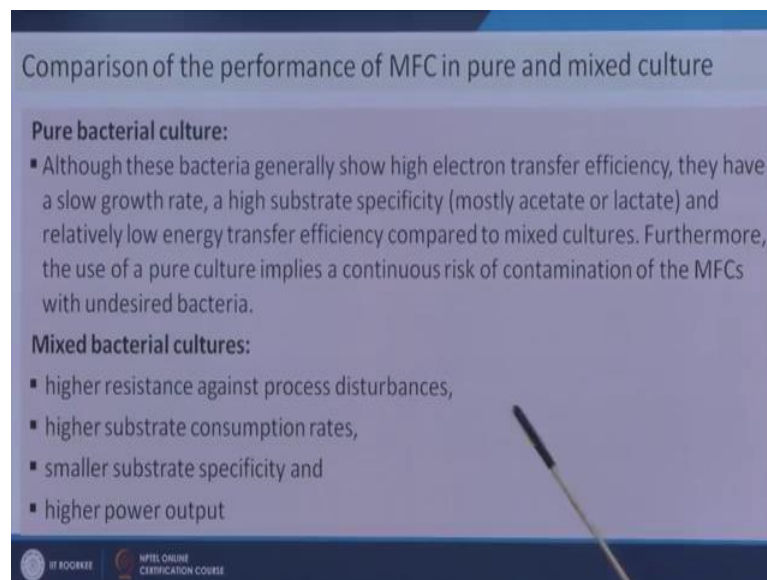
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Micro-organism	Substrate	Anode	Current (mA)	Power (mW/m ²)	Reference
Mixed seawater culture	acetate	graphite	0.23	10	Bond et al. 2012
	sulphide /acetate	graphite	60	32	Tender et al. 2012
Mixed active sludge culture	acetate	graphite	5	-	Lee et al. 2013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

Similarly, the mixed seawater culture mixed activated sludge culture has also been reported and different types of substrate have been used and anode material current

productions. So, these are reported by these authors now from this table. It is very clear to us that either pure microbial culture or mixed culture can be used and this may be substrate may be pure substrate or may be waste water also some waste waters have been also been tested by these microbial fuel cell theory, but this is not included here.

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Comparison of the performance of MFC in pure and mixed culture

Pure bacterial culture:

- 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 a pure culture implies a continuous risk of contamination of the MFCs with undesired bacteria.

Mixed bacterial cultures:

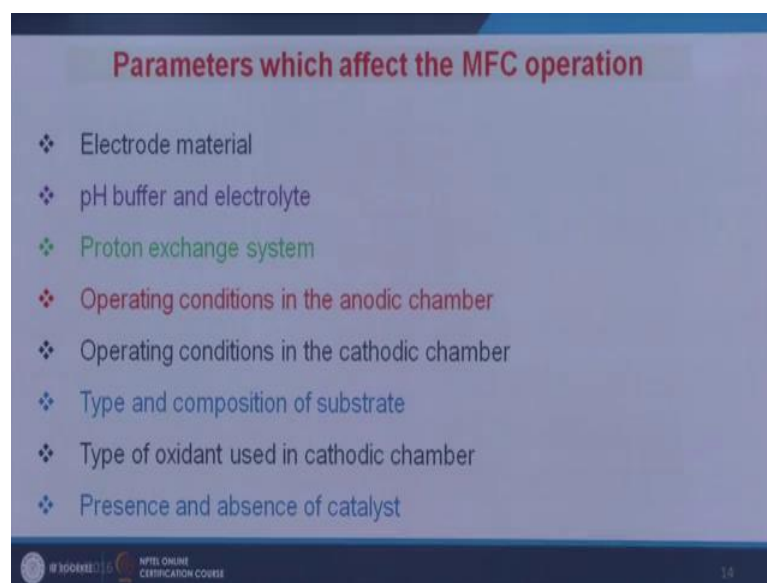
- higher resistance against process disturbances,
- higher substrate consumption rates,
- smaller substrate specificity and
- higher power output

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So, if we use the mix bacterial culture then that can give us higher resistance against process disturbances. So, those are more suitable for production of electricity and higher power output we can get from the mixed bacterial cultures we can get smaller substrate specificity; that means, variety of substrates can be available in the waste water and we can use mixed bacterial culture.

So, that all the substrates will be simultaneously degraded, but in case of pure bacterial culture it has some disadvantage that is very specific to substrate same microorganisms may not be equally effective for all type of organic compounds, but it has some advantage that it is relatively high electron transfer efficiency.

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Now, we will see the parameters which affect the MFC operations the microbial fuel cell is dependent on number of parameters one is electrode material. So, electrode material influences the performance of it because electron transfer takes place through the anode; so here the anode. So, electron transfer takes place.

So, pH buffer and electrolyte, so here the anode; so electron transfer takes place. So, pH buffer and electrolyte pH buffer is required because to maintain the pH. So, microbes require a certain pH for their growth and microbial activities and electrolyte also helps the transfer of electron and also the growth of the microorganisms. So, photon exchanges system more the effective photon extent systems we will be able to reduce the losses photon losses. So, the performance of the system will improve operating conditions in the anodic chamber anodic chamber operating conditions, we have certain types of microorganisms.

So, a toxic conditions and any pH conditions or other conditions presence of toxic elements in the solutions all those things the operating conditions in the anodic chamber is also responsible for the performance of the MFC. And operating conditions in the cathodic chamber in the same way than the operating conditions in the cathodic chamber also influences what is the catholyte, we are using etcetera will influence the performance.

Type and composition of substrate what type of substrate we are using say we have used a specific type of microorganisms which are toxic to other type of substrate like say phenolic etcetera. So, in that case the performance will vary. So, type of oxidant used in cathodic chamber I have already discussed and presence and absence of catalyst. So, if we see some catalyst on the anode surface then the performance increases because it helps as a mediator it acts as a mediator for the transfer of electron. So, these are the factors on which the performance depends.

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Voltage and Current Calculation

Current and Charge

The current I collected at an electrode is obtained by integration of all possible local current densities i_j over the electrode surface

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

The charge (Coulombs) produced is calculated from the integration of cell current over time

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

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Now, we will see how the voltage and current calculation can be done. The current as you know is equal to current is equal to current density into area of the electrode. So, anode we have in anode if we have area of dA and i_j is the current density. So, i_j into dA if we sum up all these areas. So, then it will give us the dA into i_j .

So, this is our current generation. So, here we are 2 term we are getting one is current density and another is current $i_j dA$ multiplied to sum up and then within the whole electrode area it will give us the current. And once we are getting the current then current into dt integration 0 to t is our charge. So, charge produced is calculated from the integration of this. This is the basic definition of the charge.

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Voltage and Current Calculation

Voltage and over potential

Open circuit and closed circuit voltage

Ohm's law $V_{\text{cell}} = IR_{\text{ext}}$

The Cell power (P) = $V_{\text{cell}} I$

By summation of all polarization losses, the cell voltage is written as

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

<p>Where, η = Over potential or polarization potential,</p> <p>i = Current density,</p> <p>I = Total current through the MFC</p> <p>V = Voltage (for the MFC) or potential,</p> <p>R = Electrical resistance,</p> <p>P = Microbial fuel cell power</p>	<p>E_C = electrode potential for the cathode</p> <p>E_A = electrode potential for the anode</p> <p>act = activation</p> <p>conc = concentration</p>
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And then what is the voltage and over potential. So, what is the voltage the voltage be equal to $I r$ that is we know as far ohm's law that is V_{cell} is equal to I into r external circuit. So, V equal to $I r$ when it is a closed circuit operation and then cell of power is equal to V of cell into I that current of the cell.

So, this is the power generation and this is the voltage generation in the MFC. Now a summation of all polarization losses that is equal to V_{cell} is equal to E_C minus E_A minus these are the losses. So, what is E_C and E_A that is electrode potential for the anode that is E_A electrode potential at the anode is equal to E_C , so E_C minus E_A minus other losses that will be the cell voltage. So, losses means activation losses ohmic losses and concentration, that is over potential activation over potential polarization losses and ohmic polarization losses and concentration due to concentration some loss is there and due to pH difference in anode and cathode chamber also we get some losses. So, if we subtract these losses from this it gives the V_{cell} .

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Alternatively

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

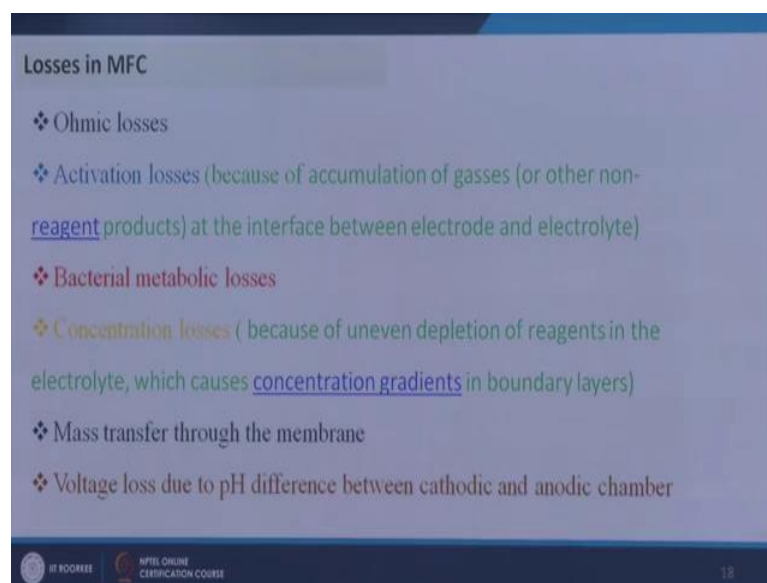
where, E_{emf} is the open circuit voltage,
 η_a is the anodic over potential
 η_b is the cathodic over potential
 $E_{\Delta \text{pH}}$ is the losses due to pH difference between cathodic and anodic solution
 E_T is the transportation loss
 E_m is the membrane loss
 E_{ionic} is the ionic loss

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Alternatively, we can write E_{cell} is equal to E_{emf} minus η_a minus η_b minus those losses η_a is the anodic over potential and η_b is the cathodic over potential and $E_{\Delta \text{pH}}$ that is $E_{\Delta \text{pH}}$ is the loss due to pH difference between anode and cathodic chamber and E_T is equal to is the transportation loss and E_{ionic} is the ionic loss and E_m is the membrane loss that will be E_{cell} is equal to E_{emf} minus η_a minus η_b minus $E_{\Delta \text{pH}}$ and minus E_T and minus E_m minus E_{ionic} ; so a membrane loss minus ionic loss. So, this is the expression we are we can get.

So, somewhere this is expressed like this and somewhere this is expressed like this.

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Now, what are the losses we have discussed that ohmic loss, concentration loss, activation loss and mass transfer loss, through the membrane and then voltage loss due to pH difference etcetera. So, what are activation losses? This activation loss is because of the accumulation of gases or other undesirable materials or products are the interface the electrode and the electrolyte. So, if we have here anode. So, in this anode the solution is there when the microbes are not being available and E minus as well as H plus is formed during the microbial activity. Well now if some gas is coming here and some material are coming here adjacent to this anode which is not desirable. So, that anode that material will prevent the exchange of electron through this the rate of exchange of electron will be reduced. So, we will be losing some current. So, that is the voltage loss that is that is due to that is called activation losses.

And now concentration loss is because of uneven depletion of reagents in the electrolyte which causes concentration gradients in boundary. So, here the concentrations are not evenly consumed the rate is varying from location to location see we do not have proper mixing this may happen. So, in that case we can get the concentration gradient in this boundary and we will be losing some voltage. So, those are the losses which we experience in the MFC mass transfer through the membrane. So, through the membrane when the transfer will take place there will be some loss mass transfer loss, and then the voltage loss due to pH difference between cathodic and anodic chamber anodic and cathodic chamber that there is slight pH difference.

So, that is why hydrogen transfer rate will be changing; that means hydrogen H^+ is present in air it is moving towards this. So, here are some pH; that means, some hydrogen concentration here is another pH. So, this is another has hydrogen concentration. So, difference in the hydrogen concentration will determine the driving force. So, it influences the transfer of hydrogen and as a whole the efficiency of the MFC.

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Types of MFC and improvement efforts

- Single chamber
- Double chamber
- Flat plate
- Membrane less MFC
- Up-flow MFC

Some efforts going on to improve the voltage and power generation in MFC are:

- Adding suitable metal ions and using metal reducing microorganisms
- Doping of catalysts on the electrode
- Increasing anode area and decreasing inter electrode distance
- Using more efficient microorganisms
- Using more suitable oxidant in cathode

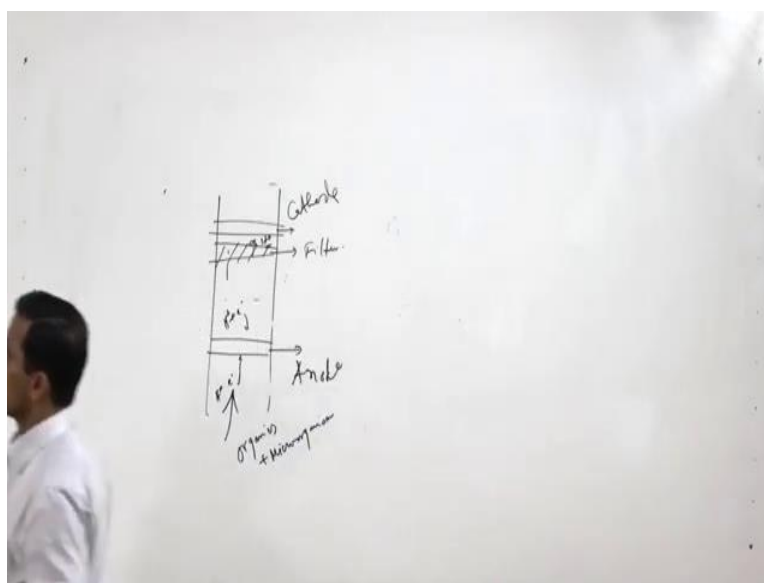
Now, we will see the types of MFC and the efforts for it are improvement. So, far different types of MFC have been reported in literature. The sum of these are reported here in this slide that is single chamber double chamber flat plate membrane less and up flow microbial fuel cell.

So, here we are getting one photograph which is showing the working of a double chamber microbial fuel cell. So, these are the electrode positions and number of electrodes are put inside this is anodic or this is cathodic. So, anodic and cathodic different number of electrodes are put and these 2 anodic and cathodic chamber has separated by one a one membrane sometimes it is membrane sometimes it is salt bridge or sometimes it is electrolyte. So, this is the working of double chamber, and single chamber we will be having only one single chamber and one anode will be there and may be the surface one cathode will be there, but in the that case that will not be there

and membrane less microbial fuel cell membrane less microbial fuel cell, there will be no membrane.

So, when membrane is replaced by say salt bridge that is also membrane less microbial fuel cell or half flow microbial fuel cell can also be a membrane less in this case the proton transfer membrane is replaced by salt bridge or even some filters also.

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So, if we have one column. So, we are putting here some electrode we are putting here some electrode. So, anode and say cathode. So, water is moving upward direction up flow. So, water organics are there plus microorganism. So, these are organics and microorganisms. So, those are going up. So, this is the anode. So, when the H plus and E minus are produced. So, those will be electrons will be moving through these directions it will go. So, here also H plus and E minus will be produced. So, electrons will come in this directions and hydrogen will goes. So, there will be some separation that will some filters. So, these fell filter will help to pass the H plus. So, this is a up flow mode of MFC.

So, these are the different types of MFC people have considered and studied and extensive work is going on to improve the performance of the MFC and some points are mentioned here some efforts are mentioned here which are investigated to improve the performance of MFC that is number one is adding suitable metal ions and using metal reducing microorganisms. So, metal ions improve the conductivity and electron transfers

and metal reducing microorganisms also helps for producing more electrons and doping of catalyst on the electrode the electrode this if it is an anode. So, some catalyst are tested are doped here to improve its performance.

Then increasing anode area and decreasing inter electrode distance. So, if the inter electrode distance is reduced in that case the transfer loss is reduced. So, that effort is going on. And an anode area if we increase though charge density it remains same then total electricity production will increase. So, increase in anode area and decrease in inter electrode distance using more efficient microorganisms. So, microorganisms are efforts are on to invent new microorganisms.

So, those will be having more potential to produce H plus and E minus ions during degradation of the organic compounds and using more suitable oxidant in the cathode. So, cathode also if we use more suitable oxidant then the electron in H plus which is coming into the cathodic chamber that will be very quickly converted to H₂O. So, as a whole the process of performance of the process will improve after this in this module.

Thank you very much for your patience.