Physics of Renewable Energy
Professor Amreesh Chandra
Indian Institute of Technology, Kharagpur
Lecture 38
Explanation of Fuel Cell Systems

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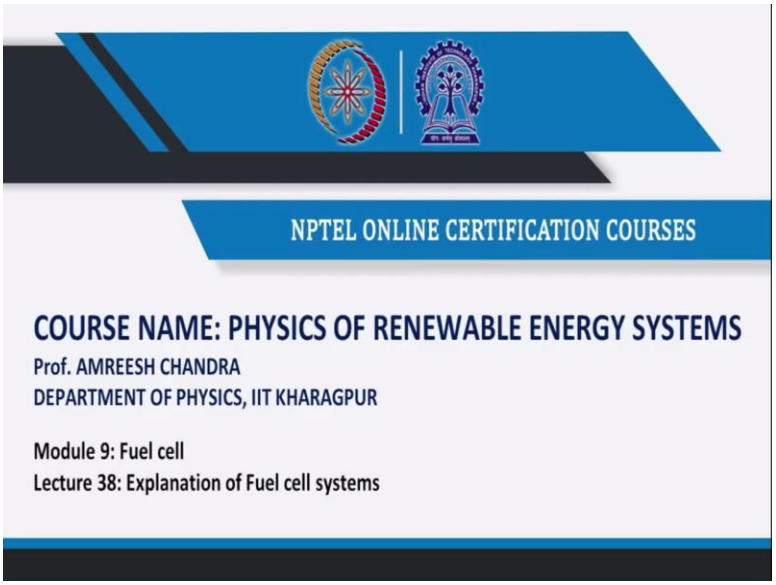

NPTEL ONLINE CERTIFICATION COURSES

COURSE NAME: PHYSICS OF RENEWABLE ENERGY SYSTEMS
Prof. AMREESH CHANDRA
DEPARTMENT OF PHYSICS, IIT KHARAGPUR

Module 9: Fuel cell
Lecture 38: Explanation of Fuel cell systems

Welcome to the second lecture on fuel cells. In the previous lecture, I gave you an overview of the technology that is the technology dealing with fuel cells. What are fuel cells? What are the reactions that are associated with fuel cells or they are occurring in fuel cells? And how do you use various types of materials to fabricate the different types of fuel cells?

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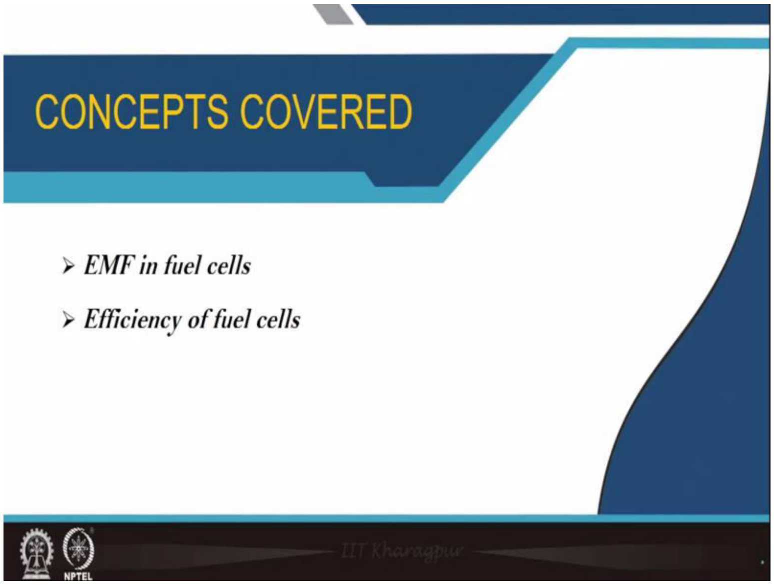

CONCEPTS COVERED

- *EMF in fuel cells*
- *Efficiency of fuel cells*

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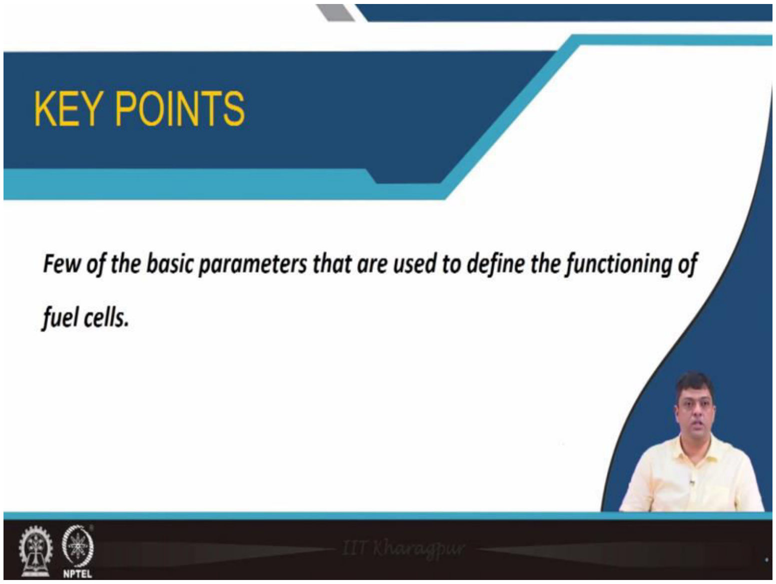

KEY POINTS

Few of the basic parameters that are used to define the functioning of fuel cells.

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In today's lecture, we will talk to you about the parameters that are used to investigate the performance of the fuel cells. What is the value of EMF that can be obtained in fuel cells? And then finally, how do you define the efficiency of a fuel cell? By the time we finish this second lecture on fuel cells, you will be understanding the basic parameters that are used to define the functioning of the fuel cell.

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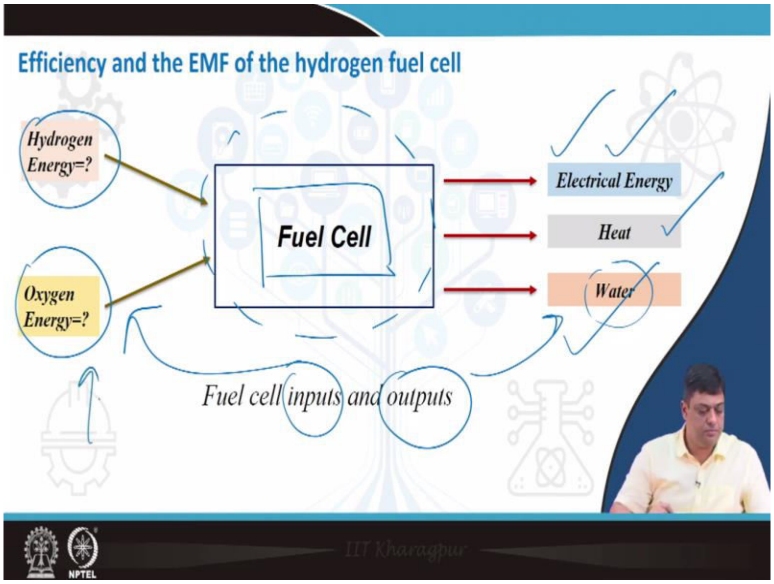

Efficiency and the EMF of the hydrogen fuel cell

Hydrogen Energy=?

Oxygen Energy=?

Fuel Cell

Electrical Energy

Heat

Water

Fuel cell inputs and outputs

So, what do you have? You have the hydrogen gas as the input then you have the oxygen which is going to react in a fuel cell. And then, what do you get? You get electrical energy; you get heat and the byproduct is water. So, you have the inputs and you have the outputs. And this is the reaction chamber in which this process is taking place.

So, what is the EMF that is, what you are going to talk in terms of electrical energy. We have already seen that losses can occur and that can be linked to the generation of heat and then the byproduct which you obtain is water. So, these are the outputs and these are the inputs.

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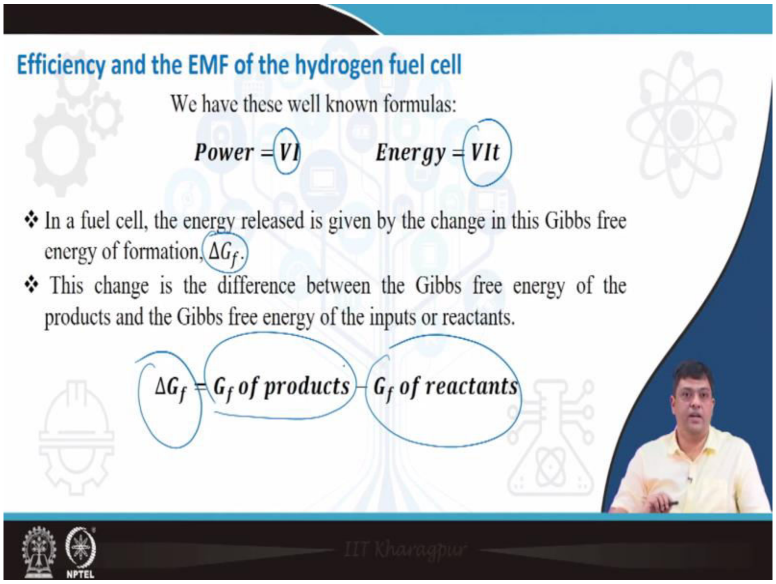

Efficiency and the EMF of the hydrogen fuel cell

We have these well known formulas:

$$Power = VI \qquad Energy = VIt$$

- In a fuel cell, the energy released is given by the change in this Gibbs free energy of formation, ΔG_f.
- This change is the difference between the Gibbs free energy of the products and the Gibbs free energy of the inputs or reactants.

$$\Delta G_f = G_f\ of\ products - G_f\ of\ reactants$$

What do we know, how do we define power? Power is V into I. Energy is equal to power into time that is V into I into t. In a fuel cell, the energy released is given by the change in this Gibbs free energy of formation that is delta Gf. This change is the difference between the Gibbs free energy of the products and the Gibbs free energy of the inputs or the reactants.

Obviously, you have the inputs, you have the outputs and therefore, what you will get energy released is the difference between the two. So, you have the Gibbs free energy which you are obtaining is the Gibbs free energy of the products minus the Gibbs free energy of the reactants.

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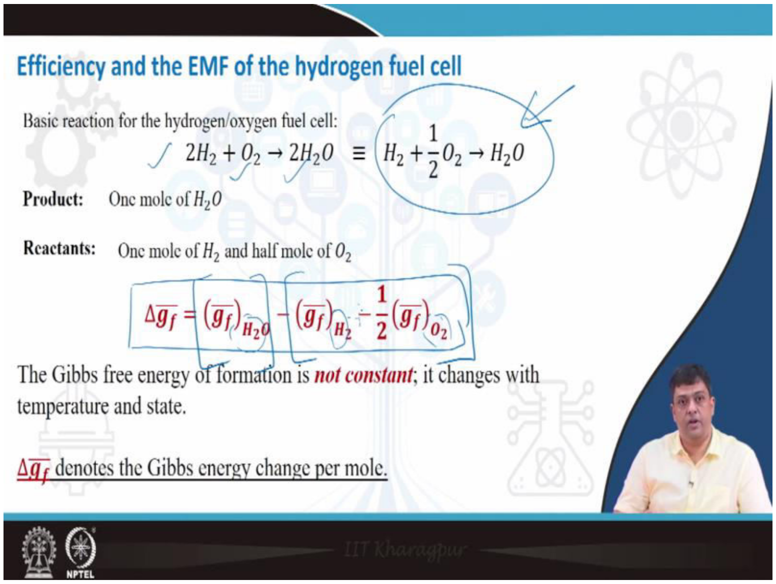

Efficiency and the EMF of the hydrogen fuel cell

Basic reaction for the hydrogen/oxygen fuel cell:

$$2H_2 + O_2 \rightarrow 2H_2O \equiv H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

Product: One mole of H_2O

Reactants: One mole of H_2 and half mole of O_2

$$\Delta\overline{g_f} = (\overline{g_f})_{H_2O} - (\overline{g_f})_{H_2} - \frac{1}{2}(\overline{g_f})_{O_2}$$

The Gibbs free energy of formation is ***not constant***; it changes with temperature and state.

$\Delta\overline{g_f}$ denotes the Gibbs energy change per mole.

Let us write the basic reactions for the hydrogen oxygen fuel cell. So, you have $2H_2$ plus O_2 giving you $2H_2O$. So, that can be written as H_2 plus half O_2 giving H_2O. Let us say you have one mole of hydrogen, H_2O. So, for one mole of hydrogen and half mole of oxygen you then write delta gf bar is equal to gf bar of H_2O minus gf bar of H_2 plus minus of half gf bar of O_2.

So, this is what you are going to get the difference between the product and the once you had considered as the input. So, this is your input side and this is your output side. But if you add a bracket then what you will have is, you will have gf bar H_2O minus gf H_2 plus of half gf bar O_2. If I do not use the bracket then the formula written just in the red color is correct.

So, please be careful with if you are using bracket or you are not using the bracket. The Gibbs free energy of formation is not a constant. It changes we know it changes with temperature and the state. And therefore, if you want to say that the Gibbs free energy change per mole will also change as a function of operating temperature and what state you are considering.

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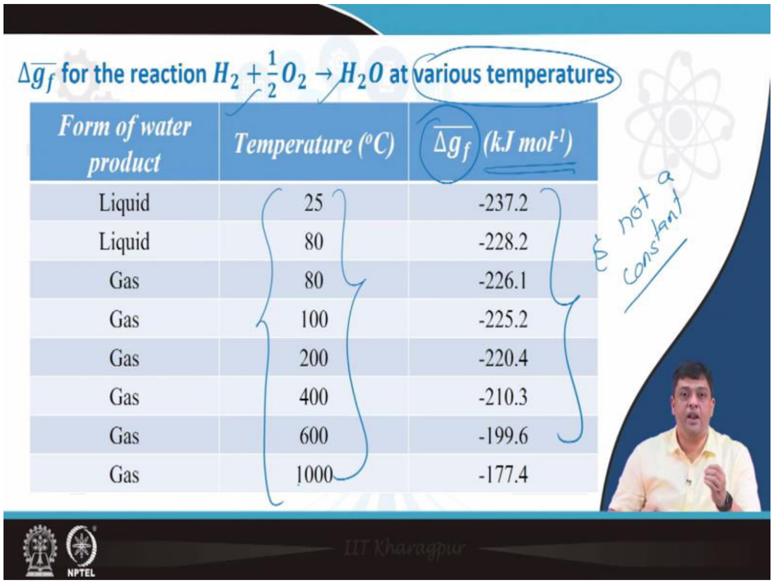

$\Delta \overline{g}_f$ for the reaction $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ at various temperatures

Form of water product	Temperature (°C)	$\Delta \overline{g}_f$ (kJ mol^{-1})
Liquid	25	-237.2
Liquid	80	-228.2
Gas	80	-226.1
Gas	100	-225.2
Gas	200	-220.4
Gas	400	-210.3
Gas	600	-199.6
Gas	1000	-177.4

& not a constant

For a reaction like H_2 plus half O_2 giving H_2O at various temperatures, so, I perform this reaction at various temperature then you can see the change in delta gf bar in units of kilojoules per mole is not a constant. It is changing and it is changing as a function of temperature. And if it is changing as a function of temperature, what can you immediately anticipate?

You can immediately understand, if you were or operate a fuel cell at different temperatures, then the output which you will obtain let us say, if you are talking about the electricity or the electrical energy which you will get would be changing as a function of temperature and that is what is called as operating temperature of the fuel cell.

So, whenever you will see certain data on fuel cells, it will be mentioning the operating temperature. And if you compare the efficiencies of the fuel cell, then please note that you should check similar types of fuel cells so, that the reactions in them are similar.

In addition, you should also check that you are comparing the performance of the fuel cell which are operating or which were made to operate at the similar temperature range because if you compare two fuel cells, which were operating at very different temperatures, then the values can be very different and you may actually end up drawing an incorrect inference.

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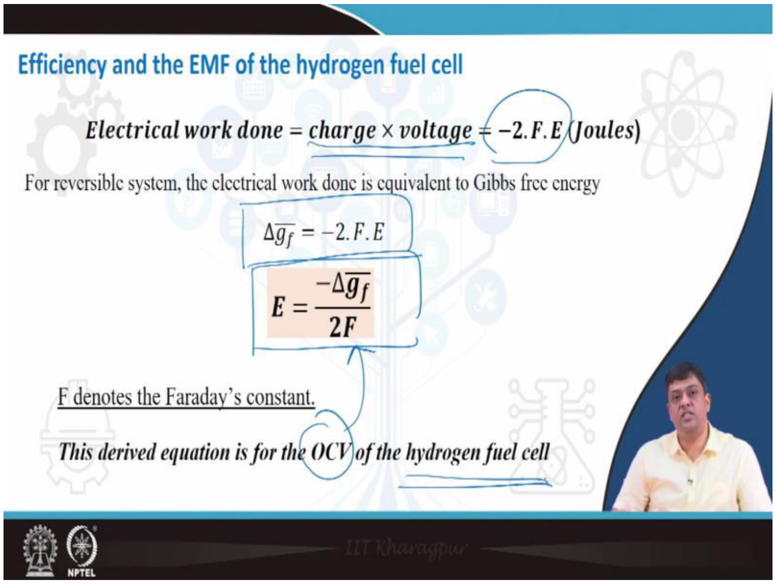

Efficiency and the EMF of the hydrogen fuel cell

$$\text{Electrical work done} = \text{charge} \times \text{voltage} = -2.F.E\ (\text{Joules})$$

For reversible system, the electrical work done is equivalent to Gibbs free energy

$$\boxed{\Delta \overline{g_f} = -2.F.E}$$

$$\boxed{E = \frac{-\Delta \overline{g_f}}{2F}}$$

F denotes the Faraday's constant.

This derived equation is for the OCV of the hydrogen fuel cell

What is the electrical work done? You know, this is charge into voltage. For a reversible reaction what happens, you have delta gf bar is equal to minus 2 Faraday's constant into E. Hence E is equal to minus delta gf bar by 2F. This equation is actually the open circuit voltage for the hydrogen fuel cell. This is what you will get as the open circuit voltage.

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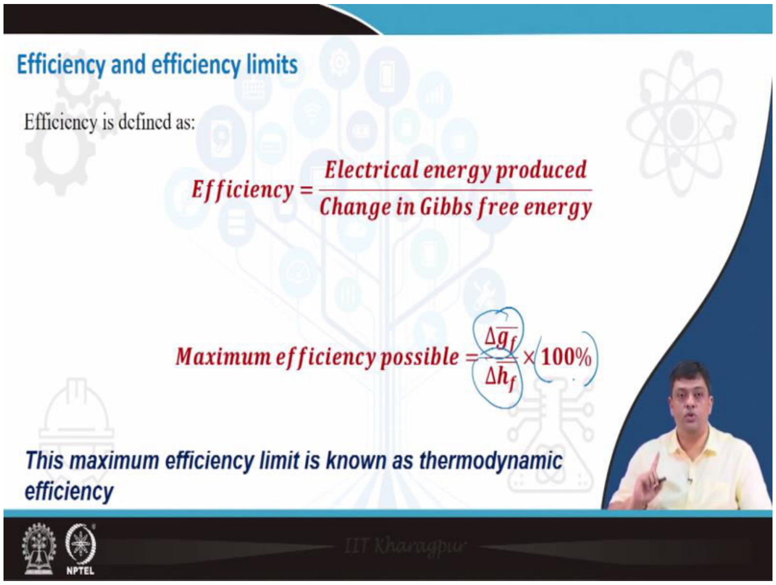

Efficiency and efficiency limits

Efficiency is defined as:

$$\text{Efficiency} = \frac{\text{Electrical energy produced}}{\text{Change in Gibbs free energy}}$$

$$\text{Maximum efficiency possible} = \frac{\Delta \overline{g_f}}{\Delta \overline{h_f}} \times 100\%$$

This maximum efficiency limit is known as thermodynamic efficiency

Efficiencies, how do you define? Efficiency is defined as the electrical energy produced divided by the change in the Gibbs free energy. So, the maximum efficiency possible is delta gf bar divided by delta hf bar in terms of percent then you multiply by 100 in terms of percent. The maximum efficiency limit is known as the Thermodynamic efficiency, this you should remember.

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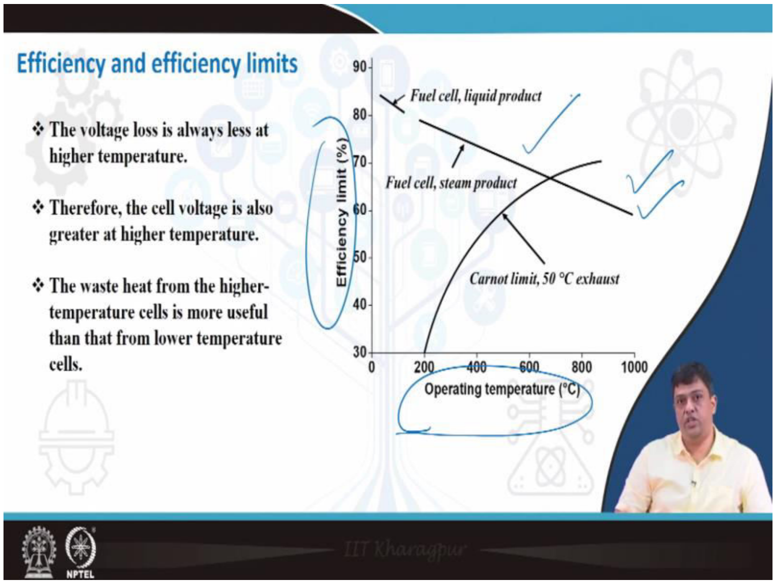

Efficiency and efficiency limits

- The voltage loss is always less at higher temperature.
- Therefore, the cell voltage is also greater at higher temperature.
- The waste heat from the higher-temperature cells is more useful than that from lower temperature cells.

And as we have seen the voltage loss is always less at higher temperatures, we have explained why that is happening. The cell voltage is also greater at higher temperatures and as a function of temperature you can see if you change the operating temperature then the efficiencies are also changing quite significantly. And the waste heat from the higher temperature cells is more useful than that from the lower temperature cells.

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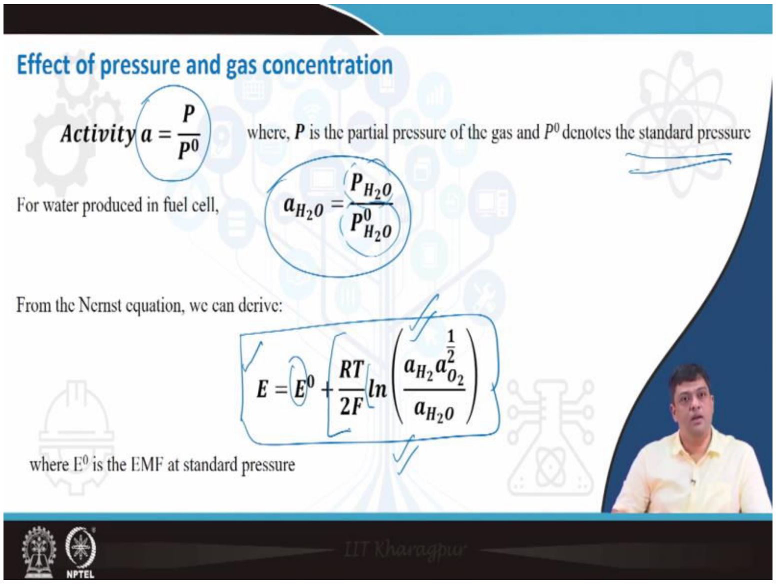

Effect of pressure and gas concentration

Activity $a = \frac{P}{P^0}$ where, P is the partial pressure of the gas and P^0 denotes the standard pressure

For water produced in fuel cell, $a_{H_2O} = \frac{P_{H_2O}}{P^0_{H_2O}}$

From the Nernst equation, we can derive:

$$E = E^0 + \frac{RT}{2F} ln\left(\frac{a_{H_2} a_{O_2}^{\frac{1}{2}}}{a_{H_2O}}\right)$$

where E^0 is the EMF at standard pressure

Now, that was a concept dealing with temperature. What is the other parameter which will come into consideration that is the pressure of the gas itself. What is the pressure of the gas that is going to interact with the electrode and the electrolyte? So, let us consider an activity which is defined as a, which is given by P by P^0 where P is the partial pressure of the gas and P^0 denotes the standard pressure.

For water producing fuel cells, you have this activity is therefore, written as P H_2O with the standard pressure P^0 of H_2O. From the Nernst equation which we have been using in the earlier classes also we can immediately write the EMF, EMF is given as E is equal to E^0 plus RT by 2F ln of which activity let us say you are talking about the hydrogen and water evolution. And so, you will have the EMF which is given as E is equal to E^0 plus RT by 2F into ln of aH_2 into aO_2 under root by the a H_2O. This is what we have been using right from the earlier classes.

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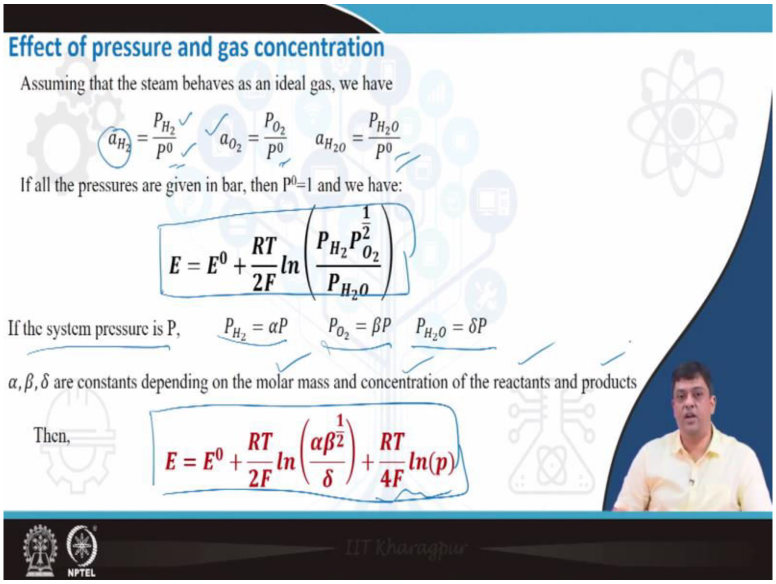

Effect of pressure and gas concentration

Assuming that the steam behaves as an ideal gas, we have

$a_{H_2} = \frac{P_{H_2}}{P^0}$ $a_{O_2} = \frac{P_{O_2}}{P^0}$ $a_{H_2O} = \frac{P_{H_2O}}{P^0}$

If all the pressures are given in bar, then $P^0=1$ and we have:

$$E = E^0 + \frac{RT}{2F} ln\left(\frac{P_{H_2}P_{O_2}^{\frac{1}{2}}}{P_{H_2O}}\right)$$

If the system pressure is P, $P_{H_2} = \alpha P$ $P_{O_2} = \beta P$ $P_{H_2O} = \delta P$

α, β, δ are constants depending on the molar mass and concentration of the reactants and products

Then,

$$E = E^0 + \frac{RT}{2F} ln\left(\frac{\alpha\beta^{\frac{1}{2}}}{\delta}\right) + \frac{RT}{4F} ln(p)$$

Now, assuming that the steam behaves as an ideal gas. So, now we are considered steam is behaving as an ideal gas. So, aH_2 is equal to PH_2 by P^0. So, ideal gas P^0. We can write aO_2 as PO_2 by P^0 and aH_2O as PH_2O by P^0. So, we are talking about in terms of ideal gas. If all the pressures are given in bars, then P^0 is equal to 1 and we have E is equal to E^0 RT by 2F ln PH_2 PO_2 raised to or half divided by PH_2O.

If the system is considered at pressure P, then PH_2 would be pressure of hydrogen would be alpha P, pressure of oxygen beta P and that of water delta P where alpha, beta, gamma are constants depending upon the molar mass and the concentration of the reactants and the product. Hence, what you will get, you will get the EMF is given by E^0 RT by 2F ln alpha beta raised to the power of half divided by delta plus RT by 4F ln p.

So, this is the EMF calculation which you can immediately calculate for a fuel cell if you know the molar mass and the concentration of the reactants and the product. So, if you write the equations, you know the molar masses and the concentration and you can calculate what is the EMF that you will obtain.

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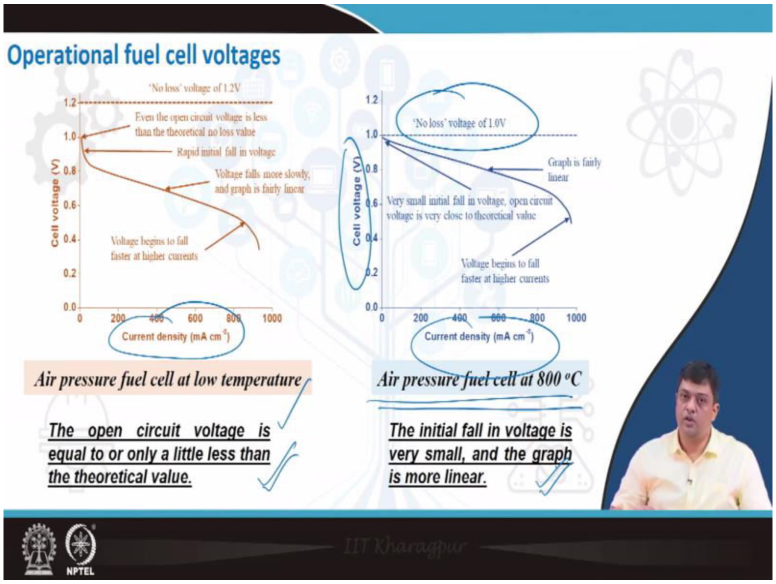

Operational fuel cell voltages

Air pressure fuel cell at low temperature

The open circuit voltage is equal to or only a little less than the theoretical value.

Air pressure fuel cell at 800 °C

The initial fall in voltage is very small, and the graph is more linear.

But, if you plot the cell voltage with current densities, then you will see that if air pressure fuel cell is at a lower temperature, then you have losses, but if you are operating at higher temperatures, then you are not seeing losses and the open circuit voltage is equal to or only slightly less than the theoretical value at low temperatures.

And in the case when you are operating at higher temperatures, the initial fall in voltage is very small and the graph is looking to be more linear. So, you know the EMF calculation, you know the operating temperature and then you can find out what would be happening to the EMF that you will obtain by working at different temperature ranges.

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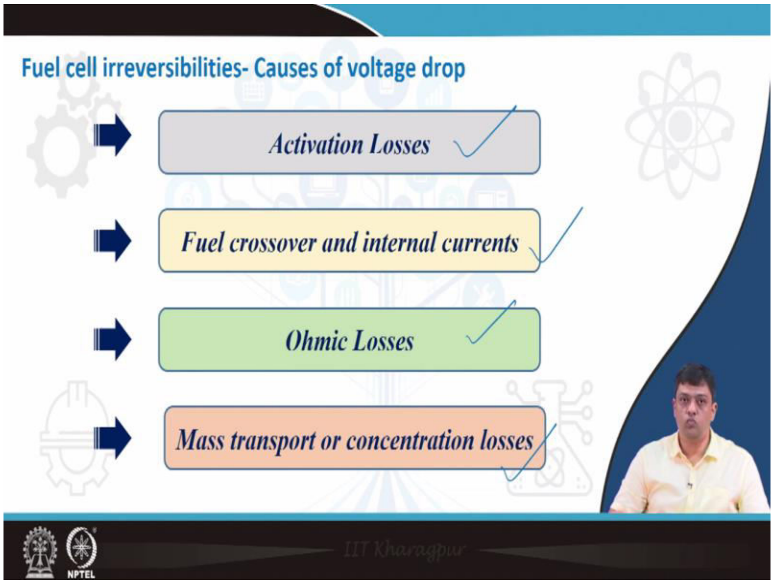

Fuel cell irreversibilities- Causes of voltage drop

- Activation Losses
- Fuel crossover and internal currents
- Ohmic Losses
- Mass transport or concentration losses

But we have seen that there are losses, these losses are associated with the activation losses, the fuel crossover and internal currents, you have ohmic losses and then you have mass transport or concentration losses. So, these are the four major losses which lead to voltage drop in the fuel cell.

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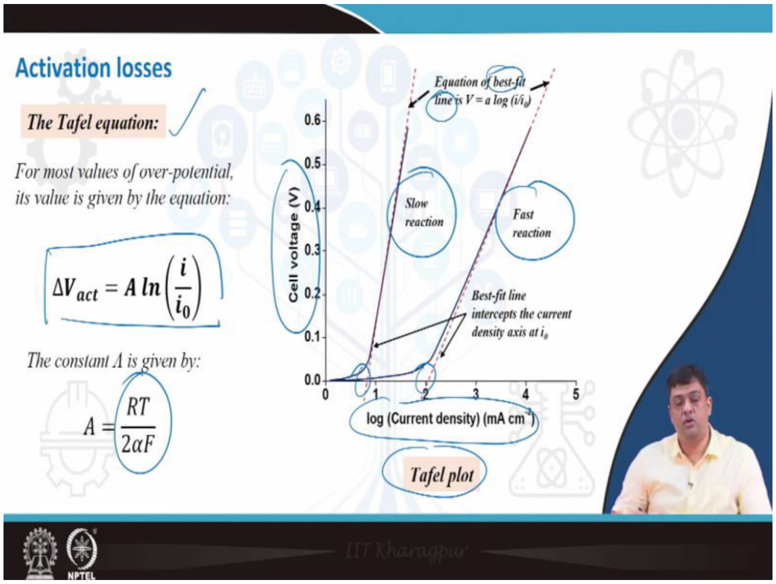

Activation losses

The Tafel equation:

For most values of over-potential, its value is given by the equation:

$$\Delta V_{act} = A \ln\left(\frac{i}{i_0}\right)$$

The constant A is given by:

$$A = \frac{RT}{2\alpha F}$$

Tafel plot

The activation losses are calculated using the Tafel equation for most values of the over potential it is given by delta V activation equals to A ln i by i_0 and the constant A is given by RT by 2 alpha F. And you can clearly see that as a function of current densities, you can have two graphs if the reactions are slow or the reactions are fast. So, then you can get very different values of current densities which are obtained by extrapolating the best fit line.

And then, you can see if you have fast reactions, then the current densities are much higher than in the case where the reactions are much slower. So, and if I ask you a question now, itself how will you increase the reaction rate? You will say either I will use catalyst or I will ensure that I am operating at a higher temperature so, that the activation barrier height can be easily overcome by the charge.

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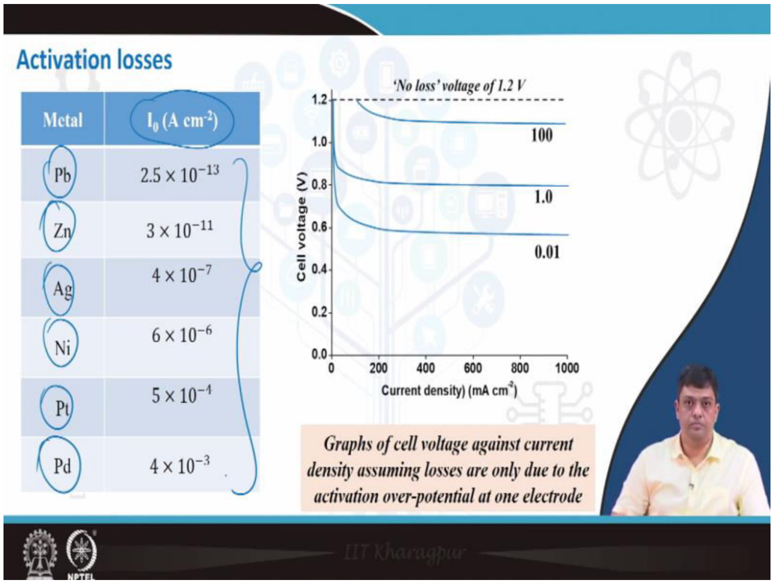

Activation losses

Metal	I_0 (A cm^{-2})
Pb	2.5×10^{-13}
Zn	3×10^{-11}
Ag	4×10^{-7}
Ni	6×10^{-6}
Pt	5×10^{-4}
Pd	4×10^{-3}

Graphs of cell voltage against current density assuming losses are only due to the activation over-potential at one electrode

So, in case you want to compare with different materials or metals in this case, then if you use different kinds of metals, then you can see that their current or the activation losses are also of different magnitude. And hence, you would like to use a catalyst or a metal which has the minimum activation loss.

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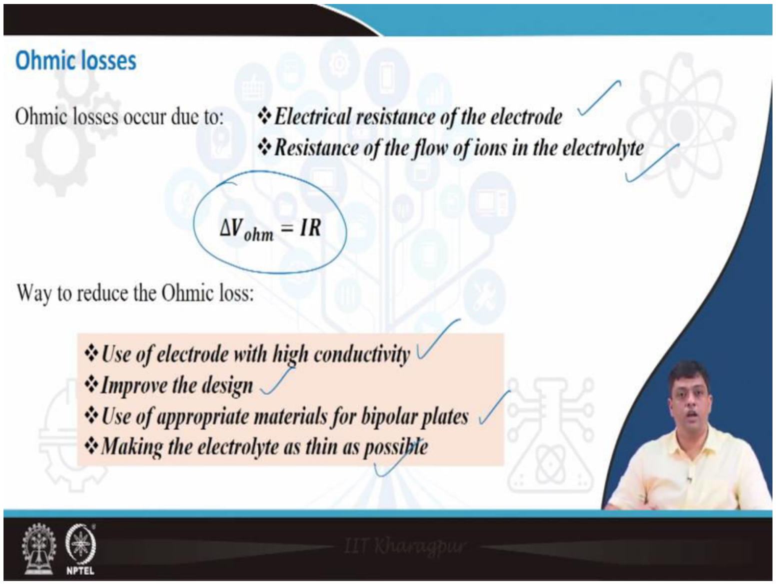

Ohmic losses

Ohmic losses occur due to:

- ❖ *Electrical resistance of the electrode*
- ❖ *Resistance of the flow of ions in the electrolyte*

$$\Delta V_{ohm} = IR$$

Way to reduce the Ohmic loss:

- ❖ *Use of electrode with high conductivity*
- ❖ *Improve the design*
- ❖ *Use of appropriate materials for bipolar plates*
- ❖ *Making the electrolyte as thin as possible*

The second thing is the Ohmic losses. This can occur because of the electrical resistance of the electrode and the resistance of the flow of ions in the electrolyte. And then that will lead to the ohmic loss that is IR. How can you reduce the ohmic losses? Very easily. You can do that you can actually use electrodes which have high conductivity, you can ensure that the flow of the electrolyte is it in a manner such that it is ensuring reduced losses when the ions transport through the electrolyte and they are also interacting with the electrode and the catalyst.

So, you need to change the configuration of the fuel cell and so, you can change the design of the fuel cell, you must use appropriate materials for bipolar plates and also because, if you can reduce the electrolyte layer then the resistance which is coming in because of the flow of this ions through the electrolyte can be reduced and then the overall ohmic losses can be reduced and hence try to make the electrolyte layer as small or as thin as possible.

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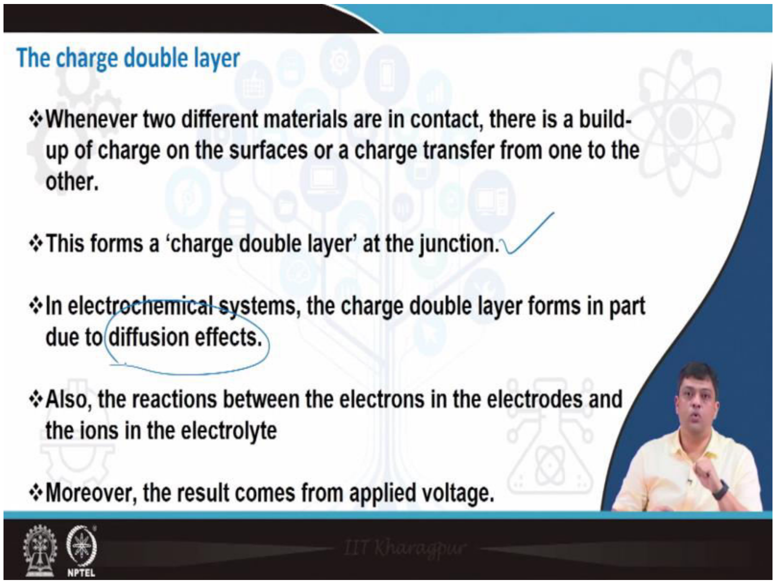

The charge double layer

- ❖Whenever two different materials are in contact, there is a build-up of charge on the surfaces or a charge transfer from one to the other.
- ❖This forms a 'charge double layer' at the junction.
- ❖In electrochemical systems, the charge double layer forms in part due to diffusion effects.
- ❖Also, the reactions between the electrons in the electrodes and the ions in the electrolyte
- ❖Moreover, the result comes from applied voltage.

Now, we have seen in the previous module that whenever two different materials are in the are brought in contact, there is a buildup of charge on the surfaces or there is a charge transfer from one to the other. If you remember double layer formation in EDLC's or you were talking about faradic reactions in pseudo capacitors and the associated formation of the parallel arrays of charges near the electrode electrolyte interface.

This charge double layer is observed at the junction of the two materials. In electrochemical systems that we have studied till now, the charged double layer forms and it is linked to the diffusion effects. Also, the reactions between the electrons in the electrodes and the ions in the electrolyte lead to the stabilization of the parallel rays of oppositely charged charges at the interface and then you will get this double layer.

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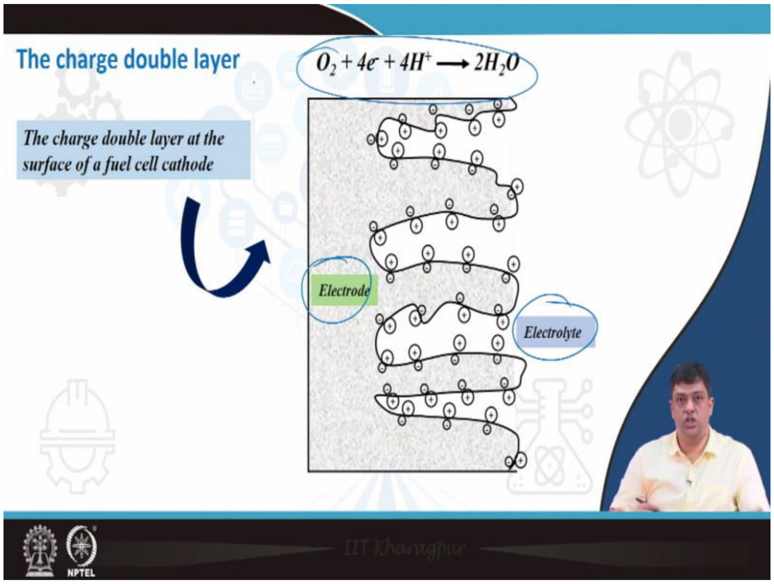

The charge double layer

$O_2 + 4e + 4H^+ \longrightarrow 2H_2O$

The charge double layer at the surface of a fuel cell cathode

So, this is what we have seen and if you see the reactions then this is what is possibly happening at the fuel cell electrode surface. You have the charged double layer at the surface of a fuel cell. So, electrolyte interacting with the surface of the electrode and that is where the charge transfer is taking place and the reactions are initiated.

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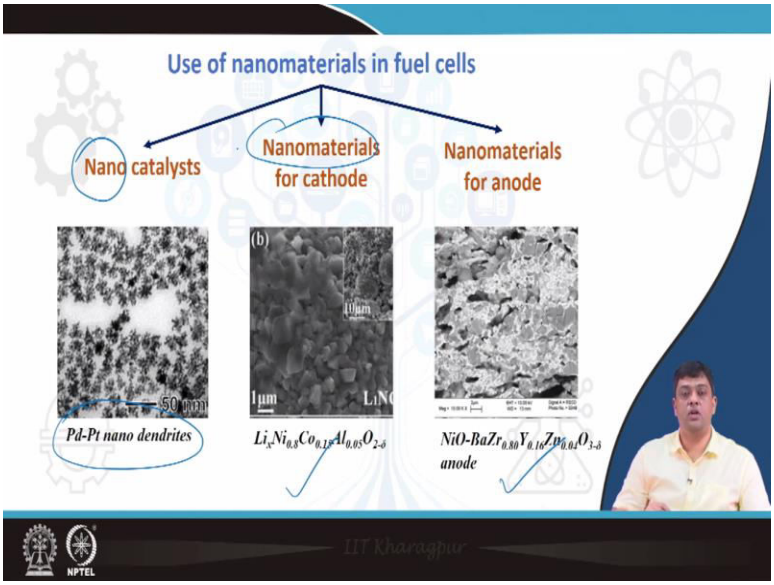

Use of nanomaterials in fuel cells

Nano catalysts

Nanomaterials for cathode

Nanomaterials for anode

Pd-Pt nano dendrites

$Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_{2-\delta}$

$NiO\text{-}BaZr_{0.80}Y_{0.16}Zn_{0.04}O_{3-\delta}$ anode

So, if I now tell you to increase the reaction rates, immediately you will say please use high surface area materials. So, what are those, those are going to be nanomaterials which have high surface to volume ratio. So, you need to use very high surface area materials both in cathode as well as in anode. These are the typical materials which are used in anode or in cathode of a fuel cell. And in addition, you please use catalysts which are there and then you can increase the reaction rate, if you can increase the reaction rate the performance can be enhanced significantly.

So, you will see that in the next module where we give you the introduction on nanomaterials, you will see that there are various types of nanomaterials, there are various strategies to prepare these materials, you can tune the surface area as per as your requirement, you can tune the porosity of these electrode materials as per the requirement of the electrode.

Why porosity because you need to send in the gas from the surroundings through the electrode so, that it can interact with the electrolyte. So, you must give pathways for the gas to diffuse in and that means you are going to introduce porous structure in these kind of materials. So, what does, what do you understand by porous structures? And how do you synthesize these porous structures?

So, it is now clear that if we are talking about systems be it be lithium-ion batteries, be it be supercapacitors, be it be fuel cells or you are talking about nano sized semiconductors for solar cells or solar based devices or use of composites in wind turbine blades, where they can have high strength but reduced weight, then we must understand the concept of nanomaterials clearly.

We must also understand the synthesis protocols of obtaining these nanomaterials and subsequently, we should understand the way we characterize these materials and that is what we will start from the next module. But as of now, we are clear that if you want to improve the reaction rate, if you want to have fuel cells, which are giving us the desired output, then the use of nanomaterials would be extensively explored in all the future fuel cell technologies or devices that are proposed.

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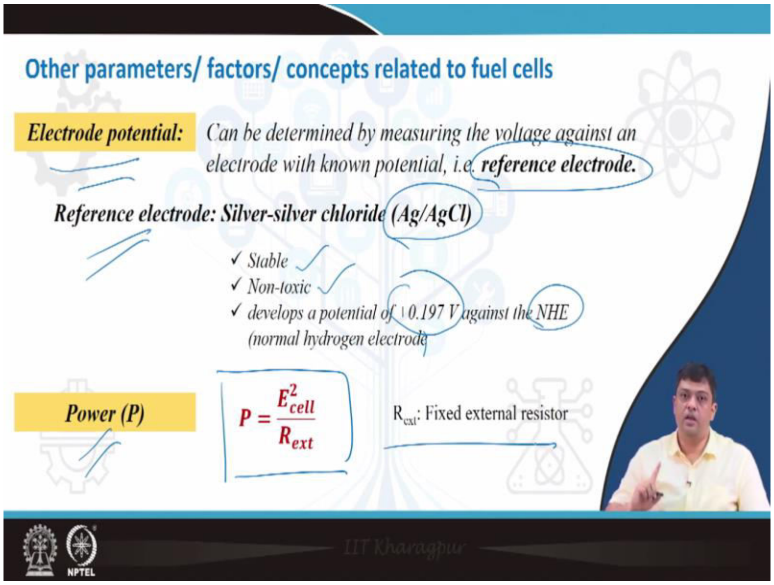

Other parameters/ factors/ concepts related to fuel cells

Electrode potential: *Can be determined by measuring the voltage against an electrode with known potential, i.e.* ***reference electrode.***

Reference electrode: Silver-silver chloride (Ag/AgCl)

- ✓ *Stable*
- ✓ *Non-toxic*
- ✓ *develops a potential of +0.197 V against the NHE (normal hydrogen electrode)*

Power (P)

$$P = \frac{E_{cell}^2}{R_{ext}}$$

R_{ext}: Fixed external resistor

There are other parameters which are essential to be understood at this point, so, that you get a better understanding regarding the working of a fuel cell. The first one is the electrode potential. The reference electrode is the next and then comes the power. So, the electrode potential can be determined by measuring the voltage against an electrode with a known potential that is the reference electrode.

And the common reference electrode which is used is the Ag, AgCl reference electrode, it is a stable reference electrode non toxic and it develops a potential of plus 0.197 volt against the normal hydrogen electrode, see the normal. So, you have a reference electrode which is developing the potential of 0.197 volt against NHE. So, now with respect to this you can find the electrode potential and the power is given by E square of the cell that is the you take the EMF of the cell take the square by R where R is the fixed external resistor.

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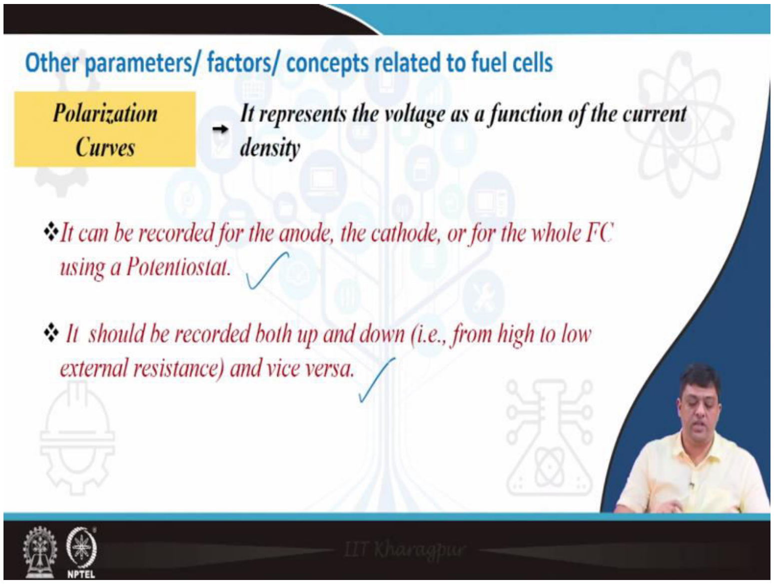

Other parameters/ factors/ concepts related to fuel cells

Polarization Curves → It represents the voltage as a function of the current density

❖ It can be recorded for the anode, the cathode, or for the whole FC using a Potentiostat.

❖ It should be recorded both up and down (i.e., from high to low external resistance) and vice versa.

Once you have obtained these parameters, you draw the polarization curves. These represent the change in the voltage as a function of current density. So, what is the parameter which are going to be used, so, you either you use voltage and next thing which you will use would be current. So, if you extract too much of current then will the voltage remain stable or if you have very high voltages, which you see stabilizing across the cell then what is the current that can be extracted.

So, using this curve you can get the optimum voltage and current that should be used or extracted from a particular fuel cell. This can be recorded for the anode, the cathode or the whole fuel cell using a potentiostat. And you will find in the module where we are talking about the CV the cyclic voltammetric or the charge discharge measurements or the impedance analysis detailed discussion on the characterization tools are given.

So, you will understand how to prepare the samples, how do you characterize, what kind of data you get and then what is the difference between a potentiostat or a galvanostat and then everything will become clear after we have given dedicated lectures on the characterization tools. Because, if you make a device and if you do not characterize it, it has no meaning whatsoever.

You must characterize it to extract the relevant information about a device and then only you can recommend the use of a system to any end user. And polarization curves must be recorded both up and down values where you are changing the resistance values from high to low or vice versa.

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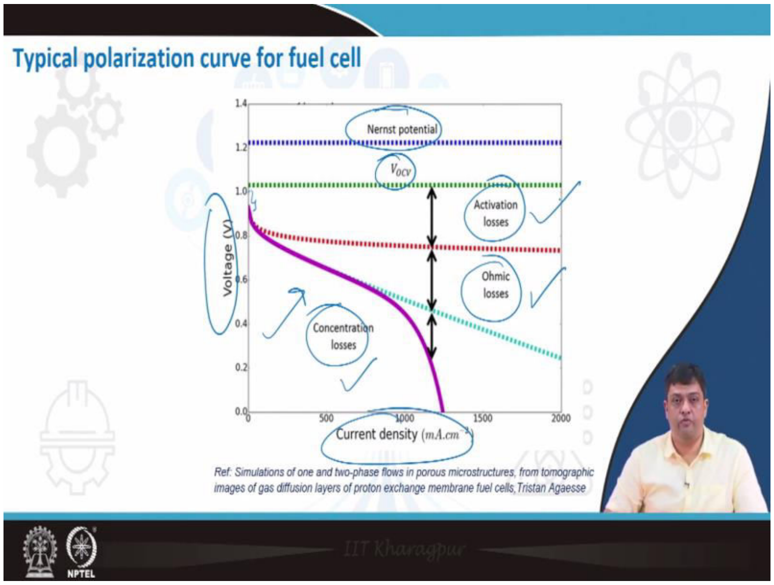

Typical polarization curve for fuel cell

Ref: Simulations of one and two-phase flows in porous microstructures, from tomographic images of gas diffusion layers of proton exchange membrane fuel cells, Tristan Agaesse

And a typical polarization curve for a fuel cells so you are having voltage as a function of current densities, you will see that this is the typical curve which you obtain you have the Nernst potential which you thought you will obtain but what you calculate is the open circuit voltage. But, when you actually operate a fuel cell, you see that there is loss in the voltage that comes in from activation losses or as you change the current densities or voltage then you have the other two losses coming into picture.

So, you can have concentration losses which are driving the change in the polarization curve. You can have ohmic losses, which are driving the loss in performance or you can have the activation losses which actually kick in right in the beginning and then they lead in the loss of the performance.

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Electrochemical characterization

Cyclic Voltammetry

- ❖ *For this measurement, either the potential or current of the electrode is varied and the complimentary electrical parameter is monitored.*
- ❖ *The potentiostat is typically operated in a three-electrode-setup consisting of a working electrode (anode or cathode), a reference electrode, and a counter electrode.*
- ❖ *In FC experiments, the potentiostatic mode is often used for voltammetry tests in which the potential of the working electrode is varied at a certain scan rate.*
- ❖ *It is also used to determine the standard redox potentials of redox active components and testing the performance of novel cathode materials.*

So, now you have calculated the power, you know what are polarization curves. And in these kind of systems, you have the electrochemical reactions which are driving the performance. So, there are various types of electrochemical characterizations, which must be performed. We have used similar kind of measurements to characterize batteries or supercapacitors, similar kind of cyclic voltammetric or charge discharge curves are used to even characterize the fuel cells. And these would be discussed in detail in the module where we talk about the characterization tools.

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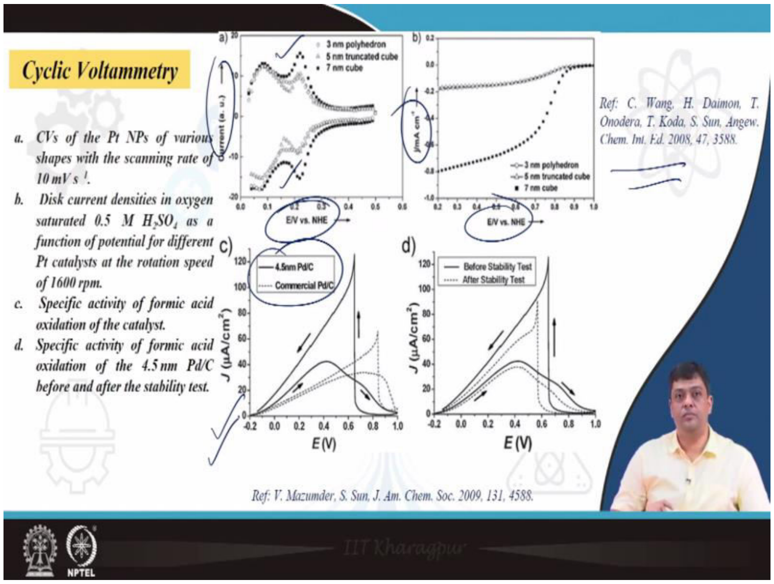

Cyclic Voltammetry

a. *CVs of the Pt NPs of various shapes with the scanning rate of 10 mV s⁻¹.*
b. *Disk current densities in oxygen saturated 0.5 M H_2SO_4 as a function of potential for different Pt catalysts at the rotation speed of 1600 rpm.*
c. *Specific activity of formic acid oxidation of the catalyst.*
d. *Specific activity of formic acid oxidation of the 4.5 nm Pd/C before and after the stability test.*

Ref: C. Wang, H. Daimon, T. Onodera, T. Koda, S. Sun, Angew. Chem. Int. Ed. 2008, 47, 3588.

Ref: V. Mazumder, S. Sun, J. Am. Chem. Soc. 2009, 131, 4588.

As I said, we will spend couple of dedicated lectures to understand what are the characterization tools that are relevant to these energy storage devices more so, the electrochemical characterization tools, but, as I said just now that you need to determine the polarization curves. So, if you look into typical polarization curves in the fuel cells, then you can clearly see that you have various kinds of nature.

And depending on the curve, you can decide what is the potential at which you will get the maximum current and that may be their recommended operating condition for a fuel cell. Depending upon the kind of catalysts you use, you can get a very different kind of a current or energy density curves. So, the use of catalyst can change the nature of the current densities or the power densities and also the temperature can change the curves which you are obtaining.

And based on these measurements, you will then recommend the operating condition for a fuel cell. So, please remember that you must clearly understand that there are various techniques that are used to characterize these fuel cells and you will have dedicated lectures to understand these techniques much more in detail.

But as of now, few things which should have become clear to you that the fuel cell performance will depend on materials, the anode material, the cathode material, the electrolyte and the catalysts and you can change or restrict the losses such as activation losses, the concentration losses or the ohmic losses by making new and normal changes in the designing of the fuel cell.

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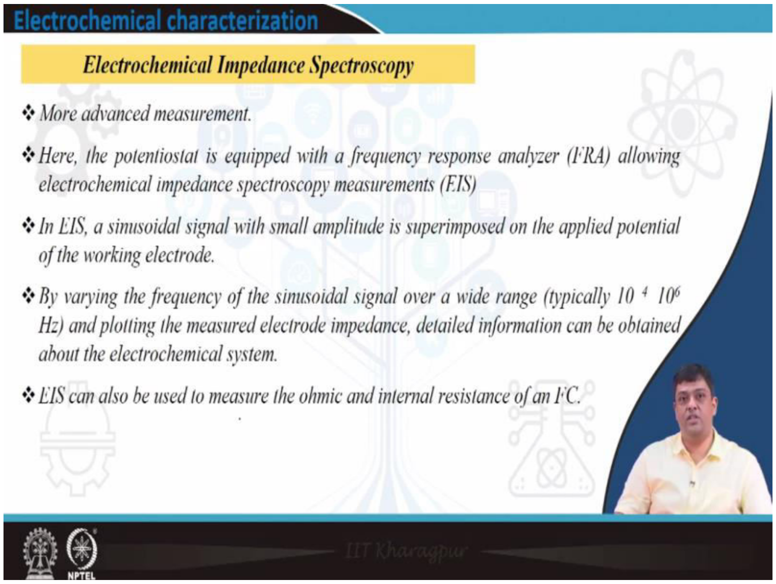

Electrochemical characterization

Electrochemical Impedance Spectroscopy

- More advanced measurement.
- Here, the potentiostat is equipped with a frequency response analyzer (FRA) allowing electrochemical impedance spectroscopy measurements (EIS)
- In EIS, a sinusoidal signal with small amplitude is superimposed on the applied potential of the working electrode.
- By varying the frequency of the sinusoidal signal over a wide range (typically 10^{-4} 10^{6} Hz) and plotting the measured electrode impedance, detailed information can be obtained about the electrochemical system.
- EIS can also be used to measure the ohmic and internal resistance of an FC.

Once you have done that, you will see that the impedance of the system will come down and the typical technique which is used to evaluate the impedance or the change in the internal resistance of electrochemical systems, right from batteries to supercapacitors to fuel cell is the electrochemical impedance spectroscopy.

Here what you do you scan the change in the impedance over a wide frequency range and then you use the Cole Cole plots to extract the information about the internal resistance or the kind of losses which are taking place which can occur at either end the interface or due to the charge transfer through the electrolyte.

So, you can obtain these information again. A dedicated lecture on electrochemical impedance spectroscopy will be given in the module where we are going to talk to you about the characterization techniques.

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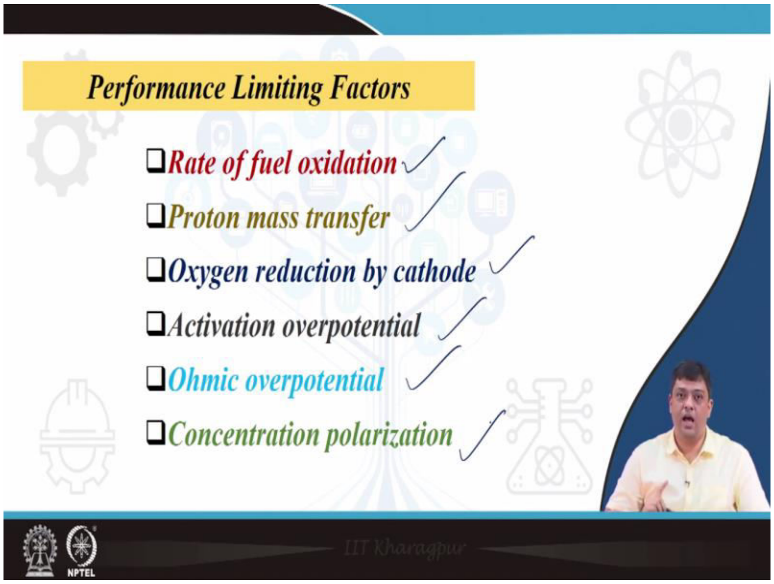

Performance Limiting Factors

- ☐ Rate of fuel oxidation ✓
- ☐ Proton mass transfer ✓
- ☐ Oxygen reduction by cathode ✓
- ☐ Activation overpotential ✓
- ☐ Ohmic overpotential ✓
- ☐ Concentration polarization ✓

The performance would therefore be restricted by the rate of fuel oxidation, proton mass transfer, oxygen reduction at the cathode, the activation over potential, ohmic overpotential and concentration polarization. So, if you can overcome these factors then or at least limit the effect of these factors in fuel cells, you will get high performing fuel cells.

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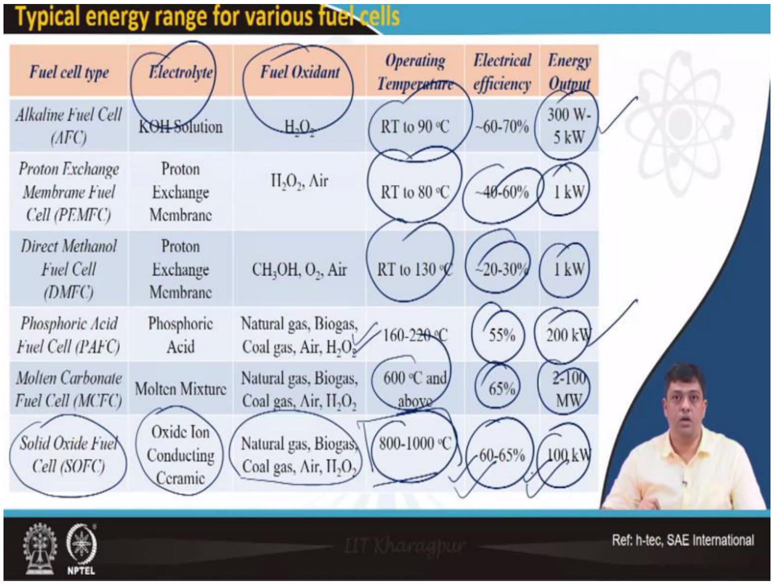

Typical energy range for various fuel cells

Fuel cell type	Electrolyte	Fuel Oxidant	Operating Temperature	Electrical efficiency	Energy Output
Alkaline Fuel Cell (AFC)	KOH Solution	H_2O_2	RT to 90 °C	~60-70%	300 W-5 kW
Proton Exchange Membrane Fuel Cell (PEMFC)	Proton Exchange Membrane	H_2O_2, Air	RT to 80 °C	~40-60%	1 kW
Direct Methanol Fuel Cell (DMFC)	Proton Exchange Membrane	CH_3OH, O_2, Air	RT to 130 °C	~20-30%	1 kW
Phosphoric Acid Fuel Cell (PAFC)	Phosphoric Acid	Natural gas, Biogas, Coal gas, Air, H_2O_2	160-220 °C	55%	200 kW
Molten Carbonate Fuel Cell (MCFC)	Molten Mixture	Natural gas, Biogas, Coal gas, Air, H_2O_2	600 °C and above	65%	2-100 MW
Solid Oxide Fuel Cell (SOFC)	Oxide Ion Conducting Ceramic	Natural gas, Biogas, Coal gas, Air, H_2O_2	800-1000 °C	60-65%	100 kW

Ref: h-tec, SAE International

And then the fuel cells will become useful and you can actually talk about obtaining fuels cells, which can give energy output in the range of let us say 300 watt to 200 kilowatt. So, you can obtain very high outputs, but then you are talking about limiting the detrimental factors which were mentioned earlier.

Again, the outputs are very high, but please note that they change as a function of temperature, they change as a function of electrolyte, they change as a function of fuel which is being supplied. And if you have very high energy outputs does, it does not mean that they will continuously have the same magnitude of efficiency. So, you may have very high outputs, but the efficiency may be lost in the overall process.

So, depending upon the use where the energy output is the consideration you may ignore the slightly reduced efficiencies, then, you are going to use let us say the phosphoric acid fuel cells, but here they are working at lower temperatures. So, depending upon the requirement of efficiency, the energy output and the operating temperature where you are going to install the fuel cell you will make the choice of the fuel cell.

For example, if you take the solid oxide fuel cell the SOFC, then you have the electrolytes where are you, you are using the oxide type ion conducting ceramics, then you can use the natural gas or the coal gas or air or H_2O_2 as the fuel oxidant. If you have SOFC is working in the range of 800 plus degrees, then the efficiencies can be quite high. In addition, the outputs can also be quite high. You can get 100-kilowatt energy output.

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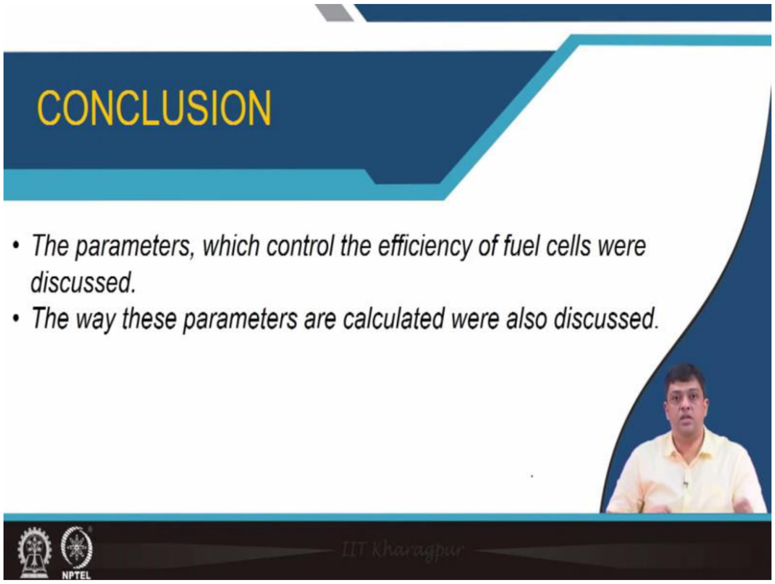

CONCLUSION

- *The parameters, which control the efficiency of fuel cells were discussed.*
- *The way these parameters are calculated were also discussed.*

So, after hearing this lecture, you must have understood the parameters which control the efficiency of fuel cells, the way you use these parameters to define the application of the fuel cells and also, we have discussed the way these parameters are calculated.

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- *Fuel Cell Systems Explained, Second Edition, J. Larminie and A. Dicks, Wiley, 2003.*
- *Need for optimizing catalyst loading for achieving affordable microbial fuel cells, I. Singh and A. Chandra, Bioresource technology, 2013, 142, 77.*
- *Use of the oxygen storage material* CeO_2 *as co-catalyst to improve the performance of microbial fuel cells, I. Singh and A. Chandra, International Journal of Hydrogen Energy, 2016, 41(3), 1913.*
- *A Comprehensive Physical Impedance Model of Polymer Electrolyte Fuel Cell Cathodes in Oxygen-free Atmosphere, M. Obermaier, A. S. Bandarenka and C. Lohri-Tymozhynsky, Scientific Reports, 2018, 8, 4933*

These are the major references from where the details were taken to prepare the lecture notes today. And in the next lecture, we will talk about, about one of the fast up and upcoming fuel cell technology that is the microbial fuel cell and also, we will talk to you about the catalysts which are becoming quite useful and then we will finish this module and from the next week, we will be moving to the module on nanomaterials. Thank you very much.