Non - Metallic Materials
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Module - 06
Optical and Electrochemical Properties of Non - Metallic Materials
Lecture - 33
Fuel Cell and Energy harvesting

Welcome to my course Non Metallic Materials and today we are in module number 6, Optical and Electrochemical Properties of Non Metallic Materials. This is lecture number 33, where I will be talking about Fuel Cell and some introduction about Energy harvesting.

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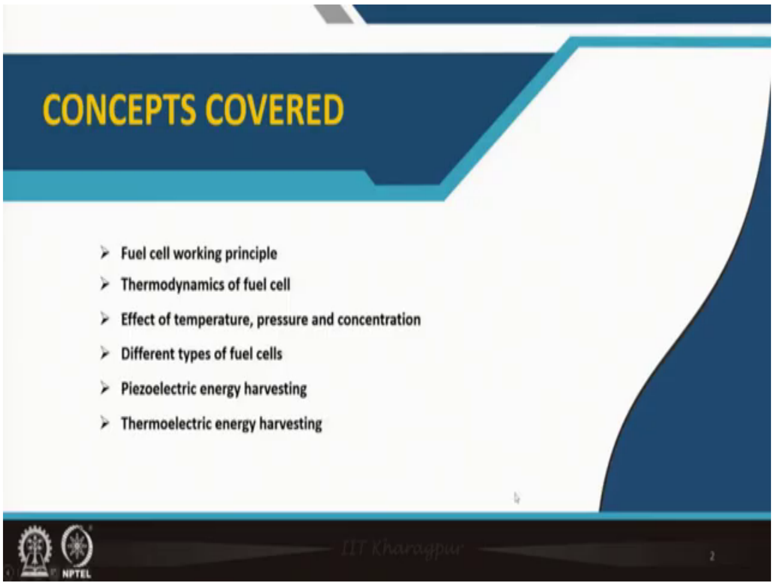

CONCEPTS COVERED

- Fuel cell working principle
- Thermodynamics of fuel cell
- Effect of temperature, pressure and concentration
- Different types of fuel cells
- Piezoelectric energy harvesting
- Thermoelectric energy harvesting

So, first we will introduce the concept of fuel cell, it is working principle and then we will have thermodynamics of fuel cell described, effect of in particular temperature, pressure and concentration that how it effects the voltage generation that will be covered, different types of fuel cell we will describe.

And in case of energy harvesting, piezoelectric and thermoelectric materials now people are using; so I will just introduce the concept how exactly they are done.

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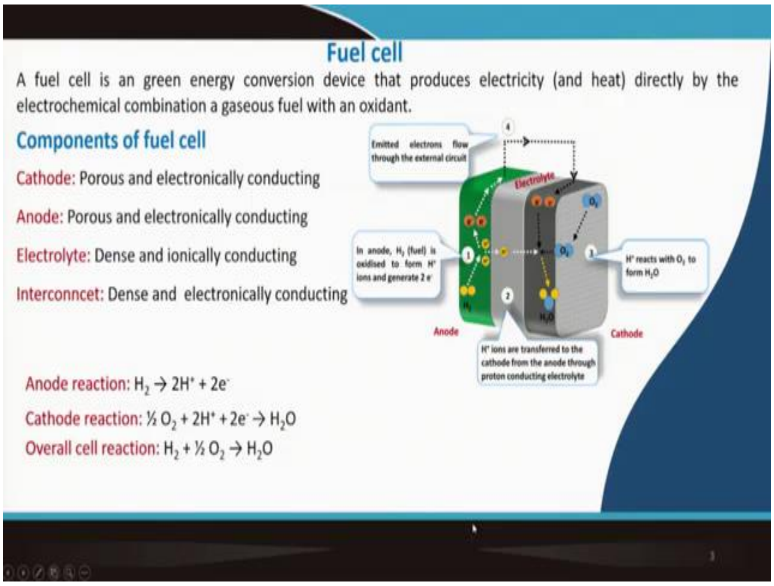

Fuel cell

A fuel cell is an green energy conversion device that produces electricity (and heat) directly by the electrochemical combination a gaseous fuel with an oxidant.

Components of fuel cell

Cathode: Porous and electronically conducting

Anode: Porous and electronically conducting

Electrolyte: Dense and ionically conducting

Interconncet: Dense and electronically conducting

1 In anode, H_2 (fuel) is oxidised to form H^+ ions and generate 2 e^-

2 H^+ ions are transferred to the cathode from the anode through proton conducting electrolyte

3 H^+ reacts with O_2 to form H_2O

4 Emitted electrons flow through the external circuit

Anode reaction: $H_2 \rightarrow 2H^+ + 2e^-$

Cathode reaction: $\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$

Overall cell reaction: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

So, a fuel cell that is a green energy conversion device that produce basically electricity. So, it is a electricity production device and already we talked about the batteries which store the energy. So, this produces electricity and additionally heat are also produced and this is by direct electrochemical combination of a gaseous fuel with an oxidant.

So, if you see the component of the fuel cell, it is having a cathode which is usually porous and they are electronically conducting. We have an anode which is also porous and electronically conducting. Electrolyte, they are usually dense and they are ionically conducting material.

And additionally we have interconnect which are also dense and electronically conducting which connects each of the cell in order to increase the generated voltage. So, in case of a hydrogen based fuel cell, the anode reaction and cathode reaction they are pretty straight forward; hydrogen is getting oxidized and it reacts with the oxygen in air and the byproduct is H 2 O, so therefore, it is a green energy generator.

And overall reaction is basically hydrogen reacts with oxygen to form water. So, if you see the construction of this fuel cell. So, in the cathode region, you have oxygen and in anode region is hydrogen is there, which is basically oxidized to form H plus ions and also generate electron which goes to the load circuit.

And this hydrogen they are transferred to the cathode from this anode region, through this proton conducting electrolyte and then it reacts with oxygen to form H 2 O as a by-product. So, this is indeed a green energy generator.

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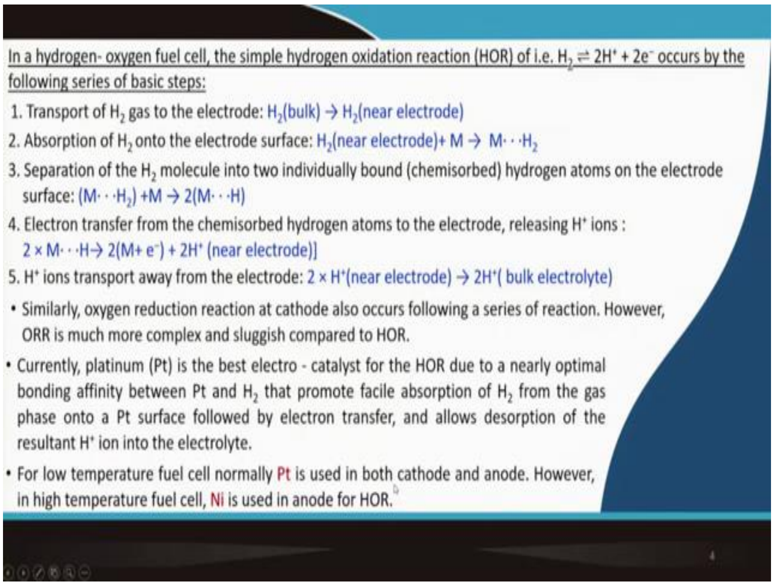

In a hydrogen- oxygen fuel cell, the simple hydrogen oxidation reaction (HOR) of i.e. $H_2 \rightleftharpoons 2H^+ + 2e^-$ occurs by the following series of basic steps:

1. Transport of H_2 gas to the electrode: $H_2(\text{bulk}) \rightarrow H_2(\text{near electrode})$
2. Absorption of H_2 onto the electrode surface: $H_2(\text{near electrode}) + M \rightarrow M\cdot\cdot\cdot H_2$
3. Separation of the H_2 molecule into two individually bound (chemisorbed) hydrogen atoms on the electrode surface: $(M\cdot\cdot\cdot H_2) + M \rightarrow 2(M\cdot\cdot\cdot H)$
4. Electron transfer from the chemisorbed hydrogen atoms to the electrode, releasing H^+ ions : $2 \times M\cdot\cdot\cdot H \rightarrow 2(M + e^-) + 2H^+ (\text{near electrode})]$
5. H^+ ions transport away from the electrode: $2 \times H^+(\text{near electrode}) \rightarrow 2H^+(\text{ bulk electrolyte})$

- Similarly, oxygen reduction reaction at cathode also occurs following a series of reaction. However, ORR is much more complex and sluggish compared to HOR.
- Currently, platinum (Pt) is the best electro - catalyst for the HOR due to a nearly optimal bonding affinity between Pt and H_2 that promote facile absorption of H_2 from the gas phase onto a Pt surface followed by electron transfer, and allows desorption of the resultant H^+ ion into the electrolyte.
- For low temperature fuel cell normally Pt is used in both cathode and anode. However, in high temperature fuel cell, Ni is used in anode for HOR.

So, if I consider a hydrogen oxygen fuel cell, the simple reaction, hydrogen oxidation reaction is hydrogen creates H plus ion and the steps that are followed are as given. So, first hydrogen is transported to the electrode, then absorption takes place hydrogen onto the electrode surface; then separation of hydrogen molecules into two individual bound hydrogen atoms on the electrode surface takes place.

Then the electron transfer from the chemisorbed hydrogen atom to the electrode and it releases H plus ions; then these H plus ions are transported away from the electrode. Similarly, in case of the cathode, oxygen reduction reaction also occurs in a series of steps.

So, as compared to the hydrogen HOR, ORR Oxygen Reduction Reactions they are very complex and also in some instances sluggish. So, usually platinum is the best electro catalyst for HOR; because of the reason that they are optimally, optimal bonding affinity between platinum and hydrogen.

That promote the easy absorption of hydrogen from the gas phase onto a platinum electrode surface, followed by this electron transfer that allows desorption of the resultant H plus into the proton conducting membrane. For low temperature fuel cell, normally platinum is used in both cathode and anode, but in case of high temperature fuel cell, nickel usually used in anode for your hydrogen oxidation reaction.

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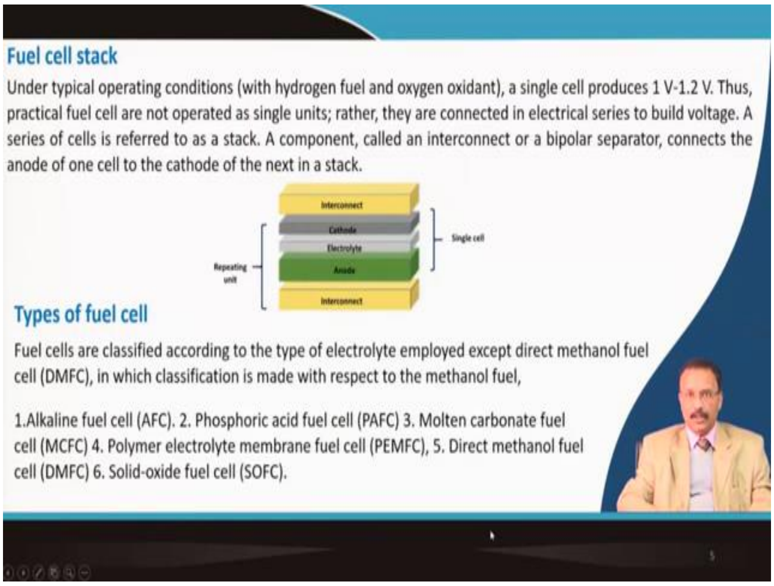

Fuel cell stack

Under typical operating conditions (with hydrogen fuel and oxygen oxidant), a single cell produces 1 V-1.2 V. Thus, practical fuel cell are not operated as single units; rather, they are connected in electrical series to build voltage. A series of cells is referred to as a stack. A component, called an interconnect or a bipolar separator, connects the anode of one cell to the cathode of the next in a stack.

Types of fuel cell

Fuel cells are classified according to the type of electrolyte employed except direct methanol fuel cell (DMFC), in which classification is made with respect to the methanol fuel,

1.Alkaline fuel cell (AFC). 2. Phosphoric acid fuel cell (PAFC) 3. Molten carbonate fuel cell (MCFC) 4. Polymer electrolyte membrane fuel cell (PEMFC), 5. Direct methanol fuel cell (DMFC) 6. Solid-oxide fuel cell (SOFC).

So, the voltage generated is in the range of 1 volt to 1.2 volt. So, practical fuel cells, they are not operated as a single unit; but they are connected in series to increase this voltage. And a series of cell that is termed as a stack, fuel cell stack. So, the component which is important is interconnect or a bipolar separator that basically connects the anode of one cell to the cathode of the next cell to complete the stack.

So, interconnect, anode, electrolyte, cathode, again interconnect and then it follows. So, there are different types of fuel cells and basically they are classified based on the type of electrolyte that is used; except in one case, that is direct methanol fuel cell, which is abbreviated as DMFC. In that particular case, the classification is made basically in terms of the fuel which is methanol.

So, apart from that, alkaline fuel cell, phosphoric acid fuel cell, molten carbonate fuel cell, polymer electrolyte membrane fuel cell they are all is having an, also solid oxide fuel cell; they are based on the electrolyte, name are based on the electrolyte which they use.

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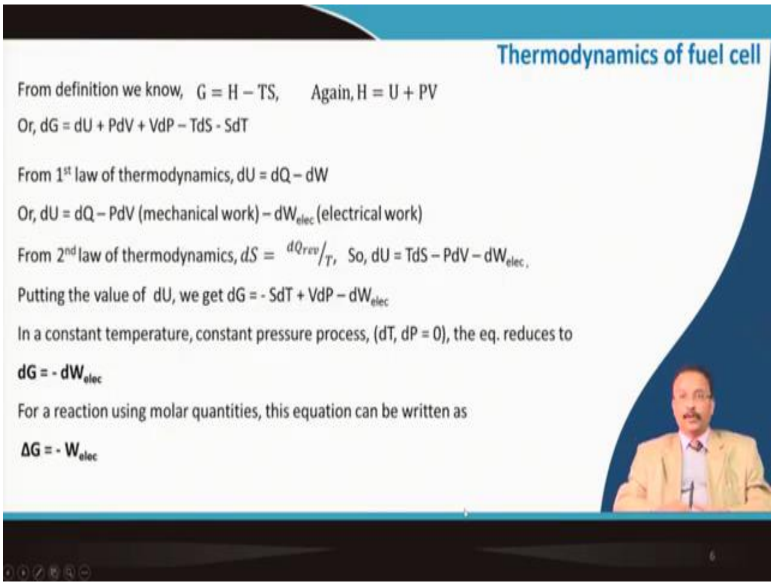

Thermodynamics of fuel cell

From definition we know, $G = H - TS$, Again, $H = U + PV$

Or, $dG = dU + PdV + VdP - TdS - SdT$

From 1st law of thermodynamics, $dU = dQ - dW$

Or, $dU = dQ - PdV$ (mechanical work) $- dW_{elec}$ (electrical work)

From 2nd law of thermodynamics, $dS = {}^{dQ_{rev}}/_{T}$, So, $dU = TdS - PdV - dW_{elec}$,

Putting the value of dU, we get $dG = - SdT + VdP - dW_{elec}$

In a constant temperature, constant pressure process, ($dT, dP = 0$), the eq. reduces to

$\mathbf{dG = - dW_{elec}}$

For a reaction using molar quantities, this equation can be written as

$\mathbf{\Delta G = - W_{elec}}$

Now, we will have to understand little bit thermodynamics to know that what kind of voltage can be generated out of these fuel cells. So, we know this basic term, the free energy is related to enthalpy, temperature and entropy. And enthalpy is related to internal energy, and pressure, and volume of the system.

So, you can differentiate this; you get d U plus PdV plus VdP minus TdS minus SdT. Now, if you apply the first law of thermodynamics, which tells you the internal energy; this dU is equal to dQ minus the work done d W. So, d U is d Q minus PdV; because this is the mechanical work which is being done minus dW electrical work.

From the second law of thermodynamics you know that the d S, the entropy difference that is dQ reversible divided by t. So, you can have dU is equal to TdS minus PdV minus dW electrical work. Now, if you put back the value of dU; you get dG is equal to minus SdT plus VdP minus dW electrical.

If you have a constant temperature and a constant pressure process, then this differential term is 0. So, your free energy change is related to the work done dG is equal to minus dW electrical. So, if you are considering a reaction using molar quantity; so this is again you can rewrite is as del G is equal to minus W electrical work.

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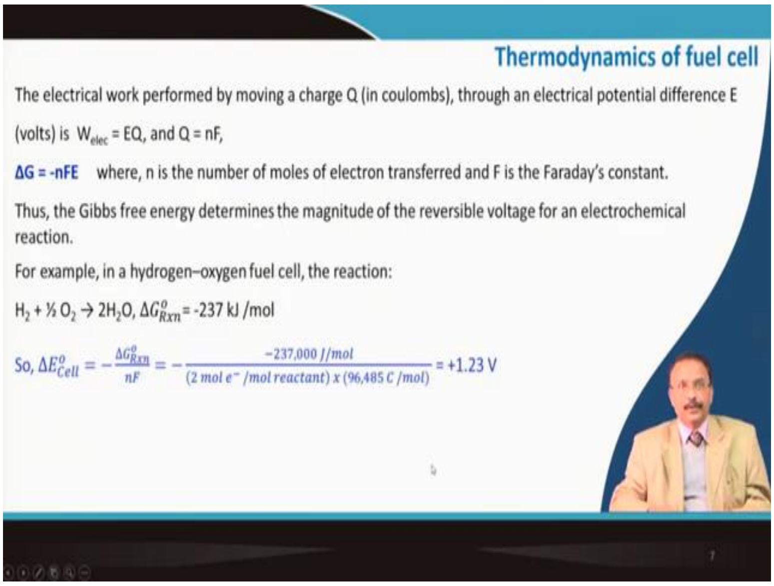

Thermodynamics of fuel cell

The electrical work performed by moving a charge Q (in coulombs), through an electrical potential difference E (volts) is $W_{elec} = EQ$, and $Q = nF$,

$\Delta G = -nFE$ where, n is the number of moles of electron transferred and F is the Faraday's constant.

Thus, the Gibbs free energy determines the magnitude of the reversible voltage for an electrochemical reaction.

For example, in a hydrogen–oxygen fuel cell, the reaction:

$H_2 + ½ O_2 \rightarrow 2H_2O$, $\Delta G^o_{Rxn} = -237$ kJ /mol

$$\text{So, } \Delta E^o_{Cell} = -\frac{\Delta G^o_{Rxn}}{nF} = -\frac{-237{,}000\ J/mol}{(2\ mol\ e^-/mol\ reactant)\ x\ (96{,}485\ C/mol)} = +1.23\ V$$

So, the electrical work that is performed by moving a charge Q, which is usually in coulomb through a electrical potential; in this case we have defined it as E. So, the W electrical is nothing, but E into Q and Q as you know that is related to n, where n is the number of moles of electron that is transferred during this reaction and F is the Faraday constant.

The same thing we have already described in one of my earlier lectures in details. So, the Gibbs free energy change, which is del G; that determines the magnitude of the reversible voltage for an electrochemical reaction.

So, if you consider this reaction, hydrogen is reacting with oxygen to form water as a byproduct. If you have the del G 0 in standard state this reaction free energy, from the table you can get this value minus 237 kilo Joule per mole.

So, your del E 0 is minus del G reaction divided by n F. So, put back this value here. So, this negative and this negative will cut. And here number of electron is 2 here per mole of the reactant and the Faraday constant you know that is 96485 coulomb per mole. So, you work it out, you will get a voltage about plus 1.23 volt.

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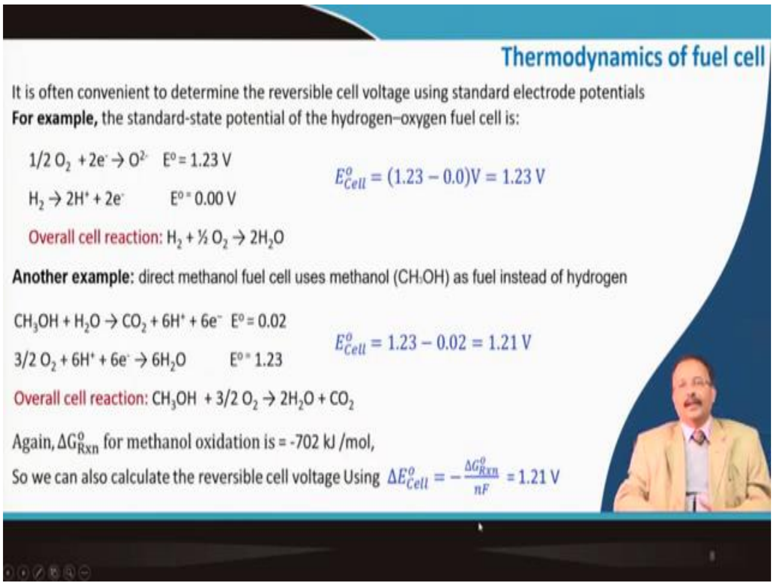

Thermodynamics of fuel cell

It is often convenient to determine the reversible cell voltage using standard electrode potentials

For example, the standard-state potential of the hydrogen–oxygen fuel cell is:

$1/2\ O_2 + 2e^- \rightarrow O^{2-}$ $E^o = 1.23$ V

$H_2 \rightarrow 2H^+ + 2e^-$ $E^o = 0.00$ V

$E^o_{Cell} = (1.23 - 0.0)V = 1.23$ V

Overall cell reaction: $H_2 + ½\ O_2 \rightarrow 2H_2O$

Another example: direct methanol fuel cell uses methanol (CH_3OH) as fuel instead of hydrogen

$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ $E^o = 0.02$

$3/2\ O_2 + 6H^+ + 6e^- \rightarrow 6H_2O$ $E^o = 1.23$

$E^o_{Cell} = 1.23 - 0.02 = 1.21$ V

Overall cell reaction: $CH_3OH + 3/2\ O_2 \rightarrow 2H_2O + CO_2$

Again, ΔG^o_{Rxn} for methanol oxidation is = -702 kJ /mol,

So we can also calculate the reversible cell voltage Using $\Delta E^o_{Cell} = -\frac{\Delta G^o_{Rxn}}{nF} = 1.21$ V

So, it is often convenient to determine the reversible cell voltage using simple standard electrode potential; already I described it in part of my earlier lectures. So, standard state potential for hydrogen oxygen fuel cell if you calculate; then the reaction here oxygen is taking the electron to form oxide this O 2 minus ion. So, that is about 1.23 volt. And hydrogen in standard case is 0.

So, the value will be 1.23 minus 0, so about 1.23 volt. So, overall cell reaction also you can see it is given, just to illustrate that the byproduct is water, which is energy; I mean environmental friendly as compared to the burning of fossil fuel, you get lot of other gases, which are not good for the ambience.

If you take another example, say in case of direct methanol fuel cell; what is used as a fuel instead of hydrogen, then also your standard E 0 value is 0.02 and in this reaction, the standard potential is 1.23. So, it is right away coming as 1.1 volt. So, if you start to calculate it based on the free energy which just I described; so that value for methanol oxidation is minus 702 kilo Joule per mole.

So, we can also calculate that del E 0; that is minus of 702; so eventually it is plus and the value of N here is 6. So, you can calculate back the same result you will get about 1.1 volt.

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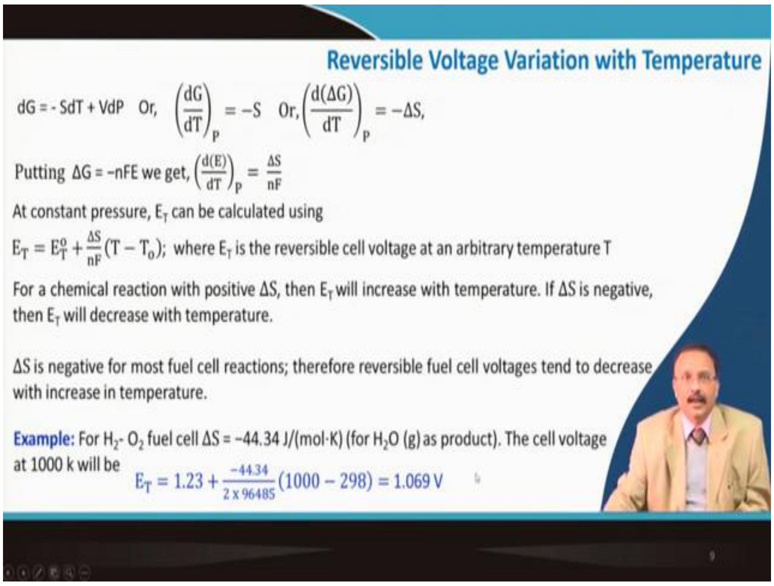

Reversible Voltage Variation with Temperature

$dG = -SdT + VdP$ Or, $\left(\frac{dG}{dT}\right)_P = -S$ Or, $\left(\frac{d(\Delta G)}{dT}\right)_P = -\Delta S,$

Putting $\Delta G = -nFE$ we get, $\left(\frac{d(E)}{dT}\right)_P = \frac{\Delta S}{nF}$

At constant pressure, E_T can be calculated using

$E_T = E_T^0 + \frac{\Delta S}{nF}(T - T_0)$; where E_T is the reversible cell voltage at an arbitrary temperature T

For a chemical reaction with positive ΔS, then E_T will increase with temperature. If ΔS is negative, then E_T will decrease with temperature.

ΔS is negative for most fuel cell reactions; therefore reversible fuel cell voltages tend to decrease with increase in temperature.

Example: For H_2- O_2 fuel cell $\Delta S = -44.34$ J/(mol·K) (for H_2O (g) as product). The cell voltage at 1000 k will be $E_T = 1.23 + \frac{-44.34}{2 \times 96485}(1000 - 298) = 1.069$ V

So, your free energy change is minus SdT plus VdP. So, if you differentiate in terms of temperature keeping the pressure constant, that is the entropy. So, if you have d of del G by dT at constant pressure, you get minus del S. So, we know this relation, del G is minus n into E into F.

So, we get this relation dE by dT at constant P; that is del S divided by number of electron into Faraday constant. So, at constant pressure, the value of E as a function of temperature, you can calculate using this relation. So, T is here the temperature and E T is the reversible cell voltage at that particular temperature.

So, for a chemical reaction with positive value of del S; then E T will increase with temperature and if del S value is negative then E T will decrease with temperature. So, for most of the fuel cell reactions, which I introduce so far; the value of del S is negative, so reversible fuel cell voltage always tend to decrease with the increase in temperature.

One example is cited here for hydrogen oxygen fuel cell; the value of del S is minus 44.34 Joule per mole Kelvin; this is for H 2 O as a product.

So, the cell voltage if you calculate at a temperature about 1000 K considering the it starts from the room temperature, you have increased the temperature to 1000; the value will get reduced because of this negative term, because your del S is negative. So, the voltage will be 1.069; in standard case, it was 1.23, so it reduces.

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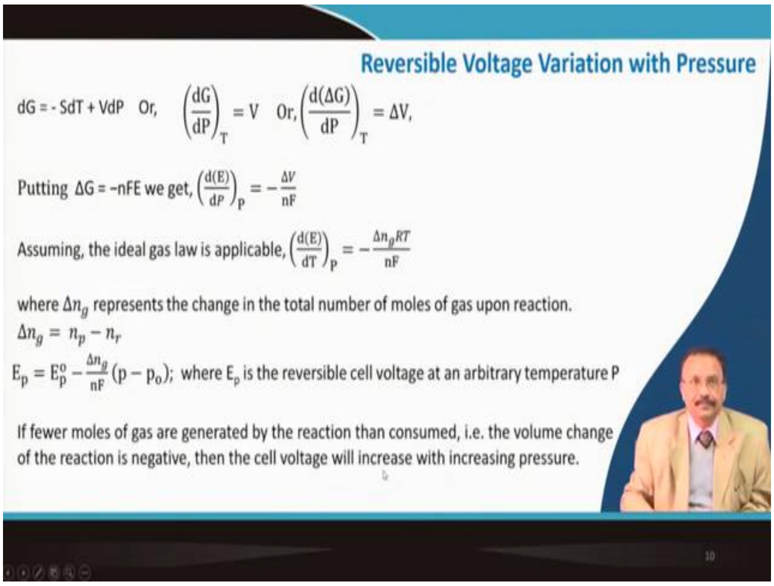

Reversible Voltage Variation with Pressure

$dG = -SdT + VdP$ Or, $\left(\frac{dG}{dP}\right)_T = V$ Or, $\left(\frac{d(\Delta G)}{dP}\right)_T = \Delta V,$

Putting $\Delta G = -nFE$ we get, $\left(\frac{d(E)}{dP}\right)_P = -\frac{\Delta V}{nF}$

Assuming, the ideal gas law is applicable, $\left(\frac{d(E)}{dT}\right)_P = -\frac{\Delta n_g RT}{nF}$

where Δn_g represents the change in the total number of moles of gas upon reaction.

$\Delta n_g = n_p - n_r$

$E_p = E_p^o - \frac{\Delta n_g}{nF}(p - p_o)$; where E_p is the reversible cell voltage at an arbitrary temperature P

If fewer moles of gas are generated by the reaction than consumed, i.e. the volume change of the reaction is negative, then the cell voltage will increase with increasing pressure.

Now, the same thing can be done for in case of a increasing pressure. So, again we have written the relevant relation and we get this value dE by dP at constant P is minus del V by nF. So, if you assume the ideal gas law, if it is applicable, then this value, this term is nothing, but del n g into the molar gas constant temperature by n into F.

Now, this term del n g that represents change in the total number of moles of gas upon the reaction. So, it is del n g is nothing but n p minus n r. So, the reversible cell voltage as an arbitrarily pressure P is given by this relation. So, if fewer mole of gas is generated by the reaction than consumed; that is the volume change of the reaction is negative, then the cell voltage will increase with increasing pressure.

So, usually that is the case; one mole of hydrogen reacts with one mole of oxygen to get H 2 O. So, here basically the volume change of the reaction will be negative; so the cell voltage you will increase little bit.

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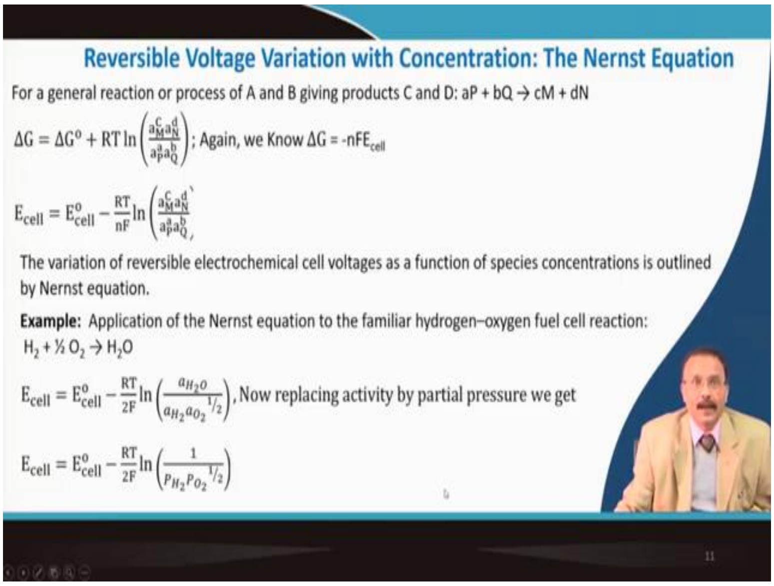

Reversible Voltage Variation with Concentration: The Nernst Equation

For a general reaction or process of A and B giving products C and D: $aP + bQ \rightarrow cM + dN$

$\Delta G = \Delta G^o + RT \ln\left(\frac{a_M^c a_N^d}{a_P^a a_Q^b}\right)$; Again, we Know $\Delta G = -nFE_{cell}$

$$E_{cell} = E_{cell}^o - \frac{RT}{nF}\ln\left(\frac{a_M^c a_N^d}{a_P^a a_Q^b}\right)$$

The variation of reversible electrochemical cell voltages as a function of species concentrations is outlined by Nernst equation.

Example: Application of the Nernst equation to the familiar hydrogen–oxygen fuel cell reaction:
$H_2 + ½ O_2 \rightarrow H_2O$

$E_{cell} = E_{cell}^o - \frac{RT}{2F}\ln\left(\frac{a_{H_2O}}{a_{H_2} a_{O_2}^{1/2}}\right)$, Now replacing activity by partial pressure we get

$$E_{cell} = E_{cell}^o - \frac{RT}{2F}\ln\left(\frac{1}{P_{H_2} P_{O_2}^{1/2}}\right)$$

So, for a general reaction, if you take this kind of reaction, your del G value you can calculate. Now, del G is minus n FE cell. So, E cell is given by this relation, already I have worked it out.

So, the variation of reversible electrochemical cell voltage as a function of species concentration; that is given by this Nernst relation is something related to this, which tells you the activity of H 2 O, then activity of hydrogen and the partial pressure of or the activity of oxygen.

So, eventually this activity for a relatively dilute concentration, you can replace it by partial pressure. So, your E cell value is given by this partial pressure relation.

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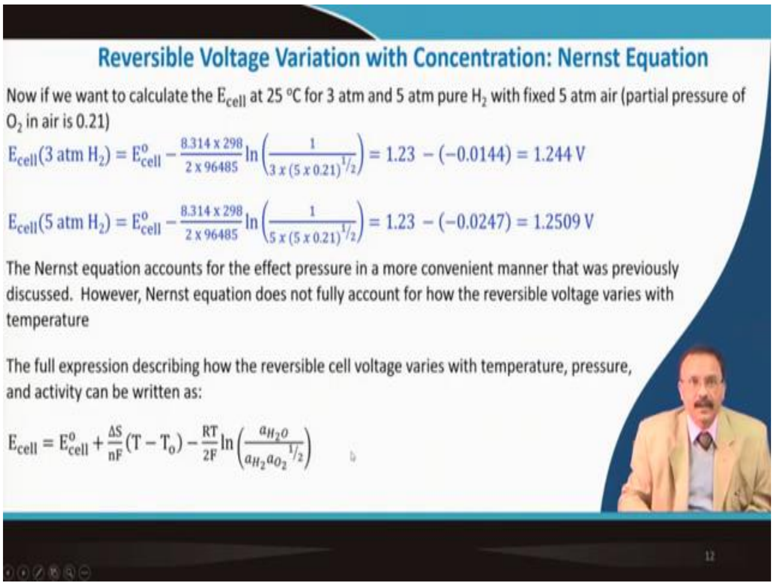

Reversible Voltage Variation with Concentration: Nernst Equation

Now if we want to calculate the E_{cell} at 25 °C for 3 atm and 5 atm pure H_2 with fixed 5 atm air (partial pressure of O_2 in air is 0.21)

$$E_{cell}(3\text{ atm }H_2) = E^o_{cell} - \frac{8.314 \times 298}{2 \times 96485} \ln\left(\frac{1}{3 \times (5 \times 0.21)^{1/2}}\right) = 1.23 - (-0.0144) = 1.244\text{ V}$$

$$E_{cell}(5\text{ atm }H_2) = E^o_{cell} - \frac{8.314 \times 298}{2 \times 96485} \ln\left(\frac{1}{5 \times (5 \times 0.21)^{1/2}}\right) = 1.23 - (-0.0247) = 1.2509\text{ V}$$

The Nernst equation accounts for the effect pressure in a more convenient manner that was previously discussed. However, Nernst equation does not fully account for how the reversible voltage varies with temperature

The full expression describing how the reversible cell voltage varies with temperature, pressure, and activity can be written as:

$$E_{cell} = E^o_{cell} + \frac{\Delta S}{nF}(T - T_o) - \frac{RT}{2F} \ln\left(\frac{a_{H_2O}}{a_{H_2} a_{O_2}^{1/2}}\right)$$

So, if you want to calculate now the E cell at say 25 degree Celsius for 3 atmosphere and 5 atmosphere hydrogen. So, in fuel cell, in the fuel side, you are increasing the pressure and the other side, it is fixed with 5 atmospheric pressure, that is in the air side. And remember in air, you have 20 percent of oxygen and 80 percent of mostly nitrogen.

So, then you put it back in the earlier equation, you get the increase in the reversible cell voltage. If you increase from 3 to 5 atmospheric pressure, then again the voltage is slightly increased from 1.23 you are increasing the voltage.

So, the effect of pressure is there, I mean to increase the cell voltage; but usually there is a limit, you cannot increase the pressure to its full extent, I mean you cannot indefinitely increase it; otherwise the operational problem will be coming.

So, there is a limit and also you are not gaining the voltage that much. So, there is a limitation of increasing the voltage. So, if you consider both pressure and temperature relation, how it affects apart from the standard potential, the temperature dependence and pressure dependence, so you can calculate back the reaction.

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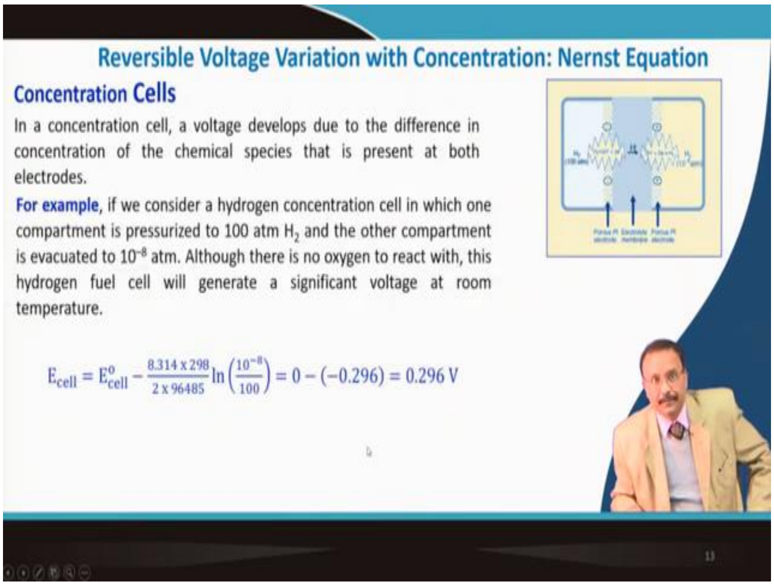

Reversible Voltage Variation with Concentration: Nernst Equation

Concentration Cells

In a concentration cell, a voltage develops due to the difference in concentration of the chemical species that is present at both electrodes.

For example, if we consider a hydrogen concentration cell in which one compartment is pressurized to 100 atm H_2 and the other compartment is evacuated to 10^{-8} atm. Although there is no oxygen to react with, this hydrogen fuel cell will generate a significant voltage at room temperature.

$$E_{cell} = E^{0}_{cell} - \frac{8.314 \times 298}{2 \times 96485} \ln\left(\frac{10^{-8}}{100}\right) = 0 - (-0.296) = 0.296\ V$$

So, just when we discussed about the electro chemical sensor part, so we talked about the concentration cell. So, if you just consider the effect of only the concentration; so only hydrogen concentration cell if you consider and it is pressurized say 100 atmospheric in one component and other component it is evacuated, so 10 to the minus 8.

So, there is no oxygen to react with, but still you will get the voltage and typically I have shown a calculation; you can get about 0.296 volt out of these concentration cells.

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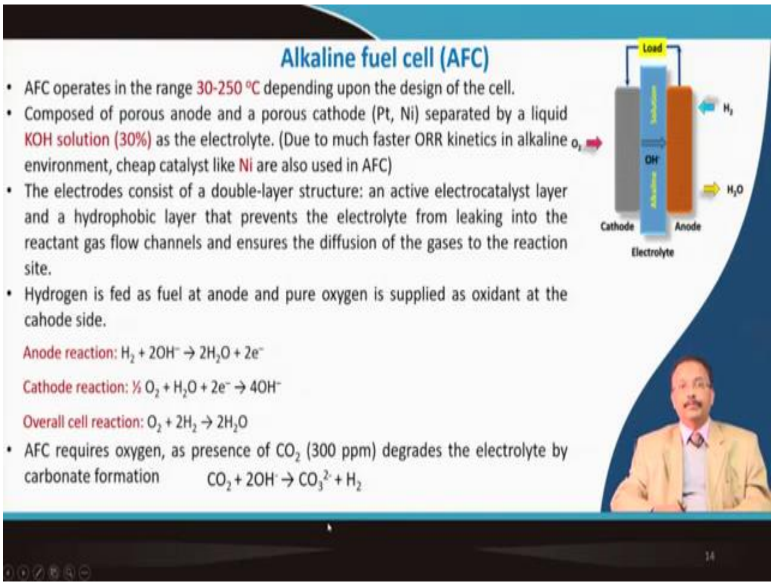

Alkaline fuel cell (AFC)

- AFC operates in the range 30-250 °C depending upon the design of the cell.
- Composed of porous anode and a porous cathode (Pt, Ni) separated by a liquid KOH solution (30%) as the electrolyte. (Due to much faster ORR kinetics in alkaline environment, cheap catalyst like Ni are also used in AFC)
- The electrodes consist of a double-layer structure: an active electrocatalyst layer and a hydrophobic layer that prevents the electrolyte from leaking into the reactant gas flow channels and ensures the diffusion of the gases to the reaction site.
- Hydrogen is fed as fuel at anode and pure oxygen is supplied as oxidant at the cahode side.

Anode reaction: $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$

Cathode reaction: $\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 4OH^-$

Overall cell reaction: $O_2 + 2H_2 \rightarrow 2H_2O$

- AFC requires oxygen, as presence of CO_2 (300 ppm) degrades the electrolyte by carbonate formation $CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2$

So, now we will talk about different types of fuel cell and I will not go into the intricate details of the formation because the operation principle they are almost same and the reaction mechanism is also same. But the operation temperature they are different, the electrolytes they are different. So, alkaline fuel cell it operates typically in a temperature range of 30 to 250 degree Celsius, depending how you are designing the cell.

So, it basically composed of a porous anode and a porous cathode, typically platinum and nickel is used, which is separated by a liquid KOH solution. And this electrode they consist of a double layer structure and active electro catalyst layer and a hydrophobic layer that, prevents the electrolyte from leaking into the reactant glass flow.

So, hydrogen is fed as a fuel in the anode and pure oxygen is fed as a oxidant in the cathode side and this is the relevant relation. And usually it requires oxygen the; because if you use air even a small quantity about 300 ppm, carbon dioxide if it is there, then carbonate will form and it will degrade the electrolyte.

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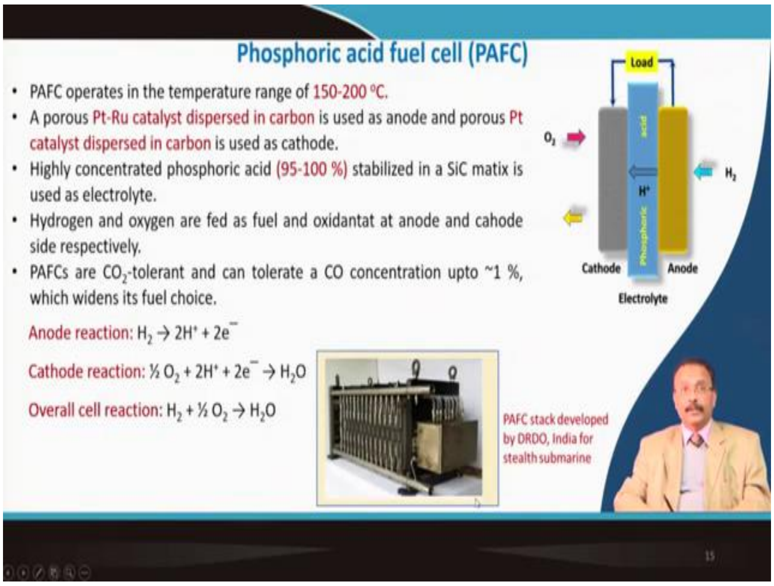

Phosphoric acid fuel cell (PAFC)

- PAFC operates in the temperature range of 150-200 °C.
- A porous Pt-Ru catalyst dispersed in carbon is used as anode and porous Pt catalyst dispersed in carbon is used as cathode.
- Highly concentrated phosphoric acid (95-100 %) stabilized in a SiC matix is used as electrolyte.
- Hydrogen and oxygen are fed as fuel and oxidantat at anode and cahode side respectively.
- PAFCs are CO_2-tolerant and can tolerate a CO concentration upto ~1 %, which widens its fuel choice.

Anode reaction: $H_2 \rightarrow 2H^+ + 2e^-$

Cathode reaction: $\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$

Overall cell reaction: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

PAFC stack developed by DRDO, India for stealth submarine

Another example is phosphoric acid fuel cell; the operating temperature range is 150 to 200 degree Celsius. Here platinum ruthenium catalyst which is dispersed in carbon is used as anode and porous platinum catalyst dispersed in carbon that is used as cathode; so, highly concentrated phosphoric acid about 95 to 100 percent which is stabilized in a silicon carbide matrix that is used as electrolyte.

Hydrogen and oxygen are fed as fuel and oxidant in anode and cathode respectively. And this is carbon dioxide tolerant and can tolerate carbon monoxide concentration about 1 percent, which basically widens its fuel choice; I am sorry, it is carbon dioxide concentration and this is the relevant reaction. So, a PAFC kind of fuel stack that has been developed in our indigenously by DEDO and that is used in submarines, stealth submarine as a power source.

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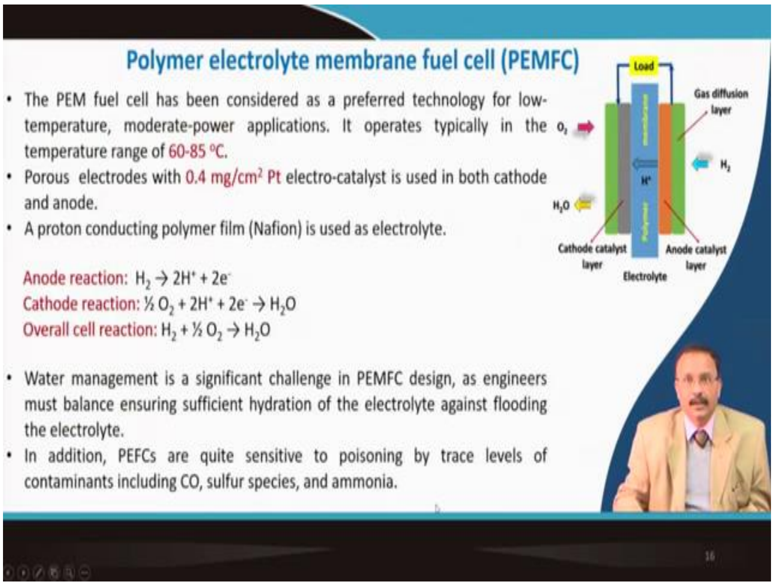

Polymer electrolyte membrane fuel cell (PEMFC)

- The PEM fuel cell has been considered as a preferred technology for low-temperature, moderate-power applications. It operates typically in the temperature range of 60-85 °C.
- Porous electrodes with 0.4 mg/cm^2 Pt electro-catalyst is used in both cathode and anode.
- A proton conducting polymer film (Nafion) is used as electrolyte.

Anode reaction: $H_2 \rightarrow 2H^+ + 2e^-$
Cathode reaction: $\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Overall cell reaction: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

- Water management is a significant challenge in PEMFC design, as engineers must balance ensuring sufficient hydration of the electrolyte against flooding the electrolyte.
- In addition, PEFCs are quite sensitive to poisoning by trace levels of contaminants including CO, sulfur species, and ammonia.

Similarly, polymer electrolyte membrane fuel cell, the operating temperature is quite low 60 to 85 degree Celsius and porous electrode typically 0.4 milligram per centimeter square, per platinum catalyst is used in both anode and cathode. And here a proton conducting polymer film is used as electrolyte. The reaction is straight forward and water management is a significant challenge for this design; because the electrolyte should not be flooded with H 2 O.

And this kind of fuel cell they are quite sensitive for poisoning; in trace level of contaminants which includes carbon monoxide, sulfur, ammonia, they can destroy the fuel cell operation. And the typical structure of this fuel cell that is illustrated schematically in this diagram.

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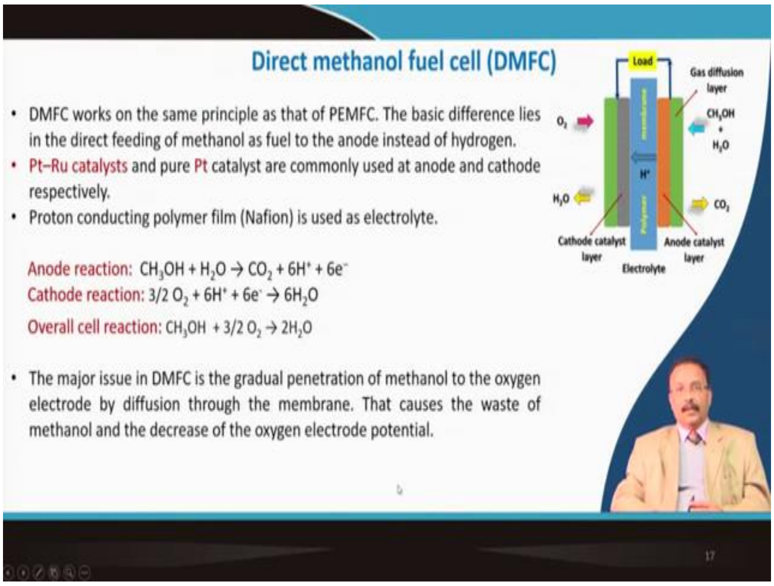

Direct methanol fuel cell (DMFC)

- DMFC works on the same principle as that of PEMFC. The basic difference lies in the direct feeding of methanol as fuel to the anode instead of hydrogen.
- Pt–Ru catalysts and pure Pt catalyst are commonly used at anode and cathode respectively.
- Proton conducting polymer film (Nafion) is used as electrolyte.

Anode reaction: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

Cathode reaction: $3/2\ O_2 + 6H^+ + 6e^- \rightarrow 6H_2O$

Overall cell reaction: $CH_3OH + 3/2\ O_2 \rightarrow 2H_2O$

- The major issue in DMFC is the gradual penetration of methanol to the oxygen electrode by diffusion through the membrane. That causes the waste of methanol and the decrease of the oxygen electrode potential.

Then we talk about direct methanol fuel cell. This basically operates in the same principle like a polymer electrolyte fuel cell, polymer membrane fuel cell. The difference that lies in the direct feeding of methanol as a fuel to the anode, instead of the usually used hydrogen; so platinum ruthenium catalyst and pure platinum catalyst, they are commonly used as anode and cathode respectively.

And proton conducting polymer film Nafion is the example that is used as electrolyte. So, the reaction is slightly different; because here you are using methanol and the major issue for this is the gradual penetration of methanol to the oxygen electrode by diffusing through the membrane and that causes the waste methanol, actually methanol is wastage due to this process and that also decrease the oxygen electrode potential.

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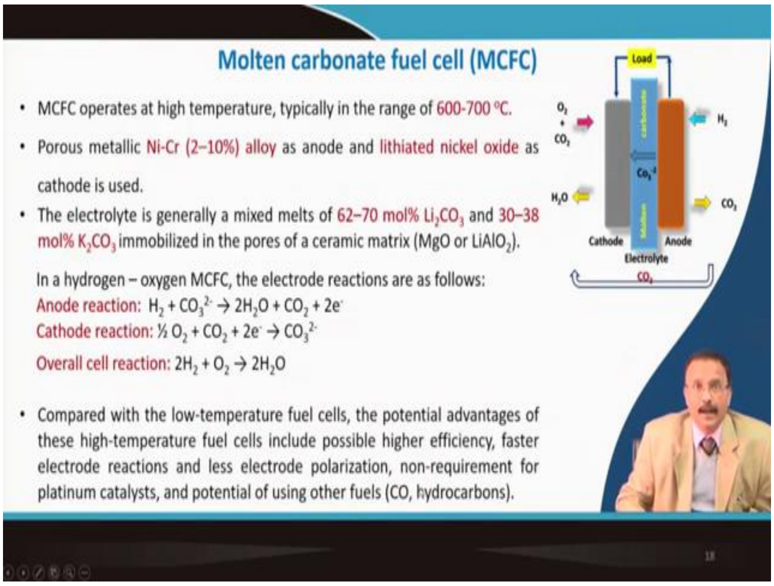

Molten carbonate fuel cell (MCFC)

- MCFC operates at high temperature, typically in the range of 600-700 °C.
- Porous metallic Ni-Cr (2–10%) alloy as anode and lithiated nickel oxide as cathode is used.
- The electrolyte is generally a mixed melts of 62–70 mol% Li_2CO_3 and 30–38 mol% K_2CO_3 immobilized in the pores of a ceramic matrix (MgO or $LiAlO_2$).

In a hydrogen – oxygen MCFC, the electrode reactions are as follows:
Anode reaction: $H_2 + CO_3^{2-} \rightarrow 2H_2O + CO_2 + 2e^-$
Cathode reaction: $\frac{1}{2} O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$
Overall cell reaction: $2H_2 + O_2 \rightarrow 2H_2O$

- Compared with the low-temperature fuel cells, the potential advantages of these high-temperature fuel cells include possible higher efficiency, faster electrode reactions and less electrode polarization, non-requirement for platinum catalysts, and potential of using other fuels (CO, hydrocarbons).

Molten carbonate fuel cell, they operate at high temperature 600 to 700 degree Celsius. And porous metallic nickel chromium alloy as used as anode and lithiated nickel oxide as the cathode material. The electrolyte is generally a mixed melt of 60 to 70 mole percent lithium carbonate and about 30 to 38 percent of K 2 C O 3 that is immobilized in the pore of a ceramic matrix, typically magnesium oxide or lithium aluminum oxide.

So, the reaction is slightly different again. So, compared to the low temperature fuel cells; the advantage of this high temperature fuel cell is that, it is higher efficiency and fast electrode reaction and usually the electrode polarization is less and this is having a potential use of other hydrocarbon into the structure.

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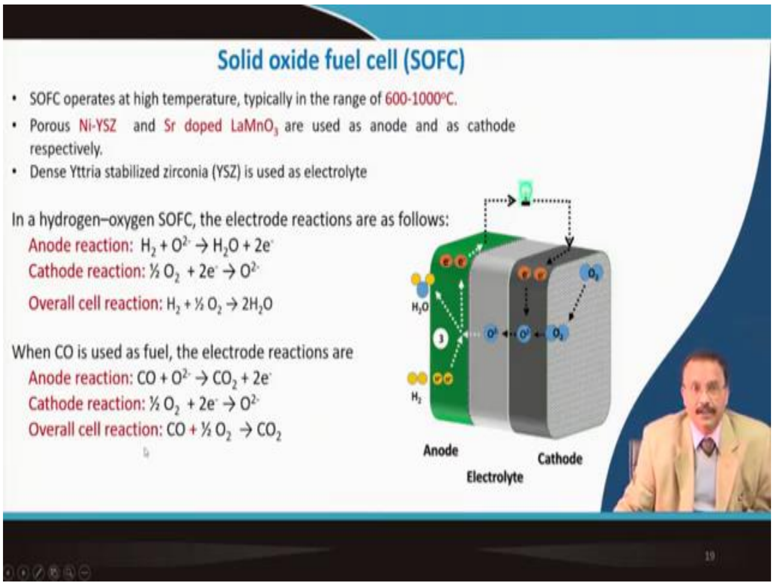

Solid oxide fuel cell (SOFC)

- SOFC operates at high temperature, typically in the range of 600-1000°C.
- Porous Ni-YSZ and Sr doped $LaMnO_3$ are used as anode and as cathode respectively.
- Dense Yttria stabilized zirconia (YSZ) is used as electrolyte

In a hydrogen–oxygen SOFC, the electrode reactions are as follows:

Anode reaction: $H_2 + O^{2-} \rightarrow H_2O + 2e^-$

Cathode reaction: $\frac{1}{2} O_2 + 2e^- \rightarrow O^{2-}$

Overall cell reaction: $H_2 + \frac{1}{2} O_2 \rightarrow 2H_2O$

When CO is used as fuel, the electrode reactions are

Anode reaction: $CO + O^{2-} \rightarrow CO_2 + 2e^-$

Cathode reaction: $\frac{1}{2} O_2 + 2e^- \rightarrow O^{2-}$

Overall cell reaction: $CO + \frac{1}{2} O_2 \rightarrow CO_2$

Solid oxide fuel cell, they uses porous nickel, yttrium stabilized zirconia and strontium lanthanum manganese oxide as anode and cathode respectively. And dense yttrium stabilized zirconia is used as electrolyte. So, in hydrogen oxygen type of SOFC, the reactions are similar. And when carbon monoxide is used as fuel; the reaction is different a bit different, but working principle is same.

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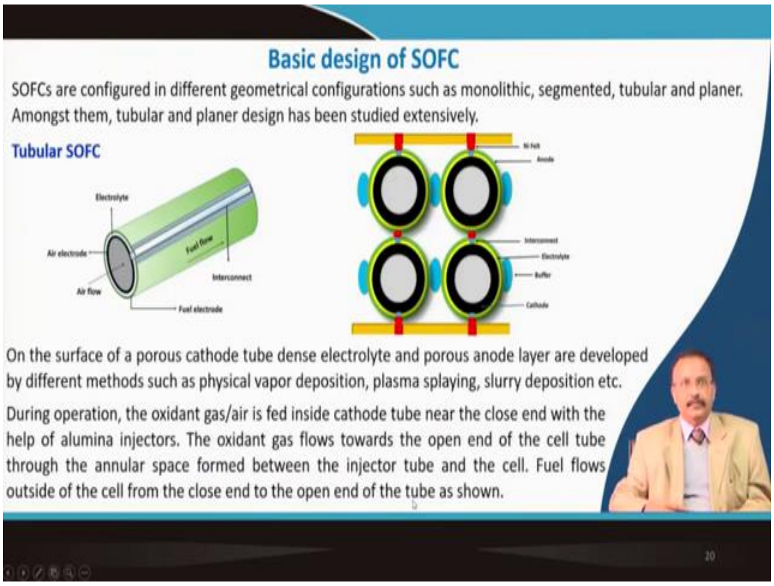

Basic design of SOFC

SOFCs are configured in different geometrical configurations such as monolithic, segmented, tubular and planer. Amongst them, tubular and planer design has been studied extensively.

Tubular SOFC

On the surface of a porous cathode tube dense electrolyte and porous anode layer are developed by different methods such as physical vapor deposition, plasma splaying, slurry deposition etc.

During operation, the oxidant gas/air is fed inside cathode tube near the close end with the help of alumina injectors. The oxidant gas flows towards the open end of the cell tube through the annular space formed between the injector tube and the cell. Fuel flows outside of the cell from the close end to the open end of the tube as shown.

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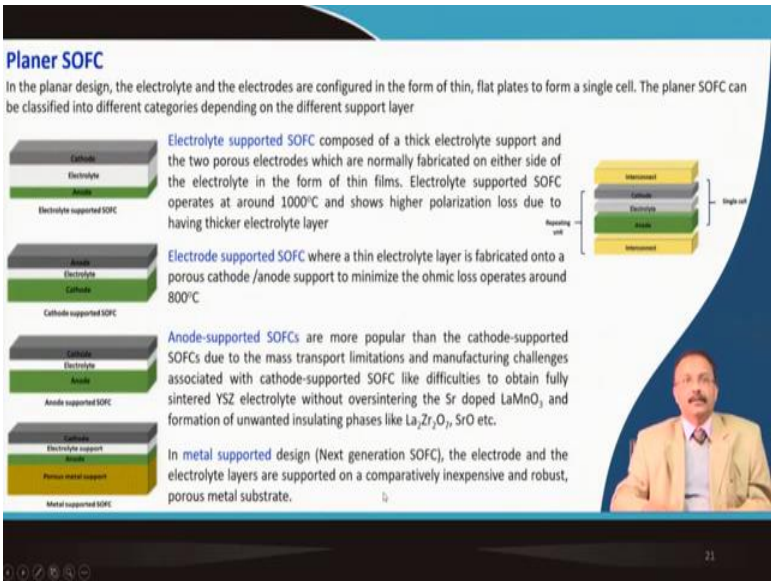

Planer SOFC

In the planar design, the electrolyte and the electrodes are configured in the form of thin, flat plates to form a single cell. The planer SOFC can be classified into different categories depending on the different support layer

Electrolyte supported SOFC composed of a thick electrolyte support and the two porous electrodes which are normally fabricated on either side of the electrolyte in the form of thin films. Electrolyte supported SOFC operates at around 1000°C and shows higher polarization loss due to having thicker electrolyte layer

Electrode supported SOFC where a thin electrolyte layer is fabricated onto a porous cathode /anode support to minimize the ohmic loss operates around 800°C

Anode-supported SOFCs are more popular than the cathode-supported SOFCs due to the mass transport limitations and manufacturing challenges associated with cathode-supported SOFC like difficulties to obtain fully sintered YSZ electrolyte without oversintering the Sr doped $LaMnO_3$ and formation of unwanted insulating phases like $La_2Zr_2O_7$, SrO etc.

In metal supported design (Next generation SOFC), the electrode and the electrolyte layers are supported on a comparatively inexpensive and robust, porous metal substrate.

Now, there are two types of design; the first one is a tubular type of SOFC and the construction you can see it here, it is given in the diagram. And another type of the design is the planar type of SOFC, which is gaining popularity. And there are basically four different types; first one is the electrolyte supported SOFC, then second one is electrode supported SOFC.

So, third one is a anode supported SOFC, and fourth one is a metal supported SOFC. So, all these designs they are trying to optimize in terms of cell performance. So, this is still in the experimental state and some commercialization of this kind of SOFC has been taken place.

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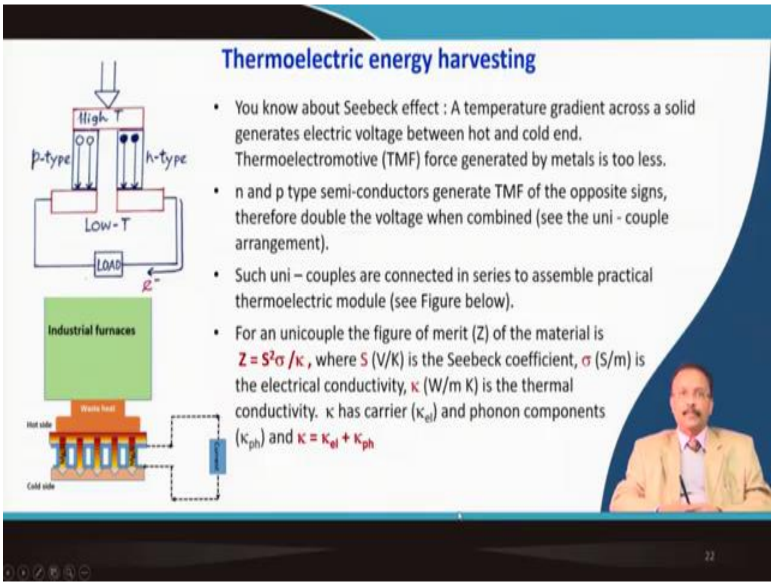

Thermoelectric energy harvesting

- You know about Seebeck effect : A temperature gradient across a solid generates electric voltage between hot and cold end. Thermoelectromotive (TMF) force generated by metals is too less.
- n and p type semi-conductors generate TMF of the opposite signs, therefore double the voltage when combined (see the uni - couple arrangement).
- Such uni – couples are connected in series to assemble practical thermoelectric module (see Figure below).
- For an unicouple the figure of merit (Z) of the material is $Z = S^2\sigma/\kappa$, where S (V/K) is the Seebeck coefficient, σ (S/m) is the electrical conductivity, κ (W/m K) is the thermal conductivity. κ has carrier (κ_{el}) and phonon components (κ_{ph}) and $\kappa = \kappa_{el} + \kappa_{ph}$

So, finally, we will introduce the energy harvesting. Already we talked about the thermoelectric material; you know about Seebeck effect, a temperature gradient across a solid generates electric voltage. So, normally metal if you use, then this voltage generation is very small.

So, usually n and p type of semiconductor, they are used in this configuration. So, this n and p type of semiconductor, they generates the thermoelectromotive force that is in opposite sign. So, therefore, they double the voltage when they are combined. So, usually this uni-couple they are connected in series assemble to use, this is shown as a schematic to increase the power generation.

And for such uni-couple the first one, the figure of merit that is defined by the Seebeck coefficient, electronic conductivity divided by thermal conductivity. So, this Seebeck coefficient is material dependent; but along with that the electronic and thermal conductivity that is also playing a major role. And the thermal conductivity that is having two term; one is due to electron, and another one is due to phonon.

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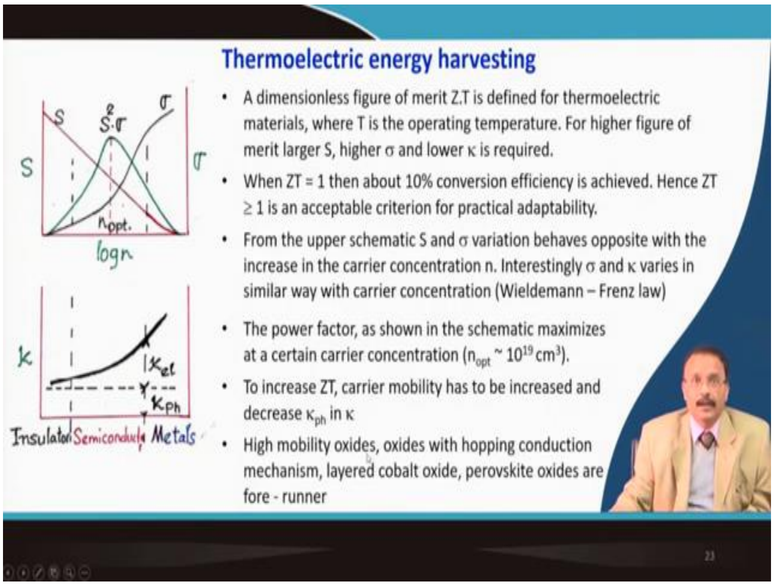

Thermoelectric energy harvesting

- A dimensionless figure of merit Z.T is defined for thermoelectric materials, where T is the operating temperature. For higher figure of merit larger S, higher σ and lower κ is required.
- When ZT = 1 then about 10% conversion efficiency is achieved. Hence ZT ≥ 1 is an acceptable criterion for practical adaptability.
- From the upper schematic S and σ variation behaves opposite with the increase in the carrier concentration n. Interestingly σ and κ varies in similar way with carrier concentration (Wieldemann – Frenz law)
- The power factor, as shown in the schematic maximizes at a certain carrier concentration ($n_{opt} \sim 10^{19}\,cm^3$).
- To increase ZT, carrier mobility has to be increased and decrease κ_{ph} in κ
- High mobility oxides, oxides with hopping conduction mechanism, layered cobalt oxide, perovskite oxides are fore - runner

So, a dimension figure of merit is usually Z into T, that is a product and that is that defines the quality of the thermoelectric material. So, of course, high figure of merit is required; but usually when ZT is equal to 1, then about 10 percent of conversion efficiency is achieved.

So, ZT more than 1 is difficult to achieve. So, the upper schematic as you can see that, the S variation with the dopant ion concentration in the semiconductor that varies oppositely. So, one is going down with the dopant concentration, another one is of course this conductivity will go up, right.

So, this power factor, this S square into sigma, that is having a peak; so that means that at a particular dopant concentration, you have the maximum value of S square into sigma. So, this power sigma, this power factor they maximize at a particular dopant concentration.

So, in order to increase the figure of merit, the carrier mobility has to be increased; because your sigma is dependent not only on the carrier concentration, but also their mobility and simultaneously we will have to decrease the thermal conductivity due to the phonon. So, high mobility oxides, oxides with hopping conduction mechanism, layered cobalt oxide, perovskite oxide they are the fore runner as far as this thermoelectric material is concerned.

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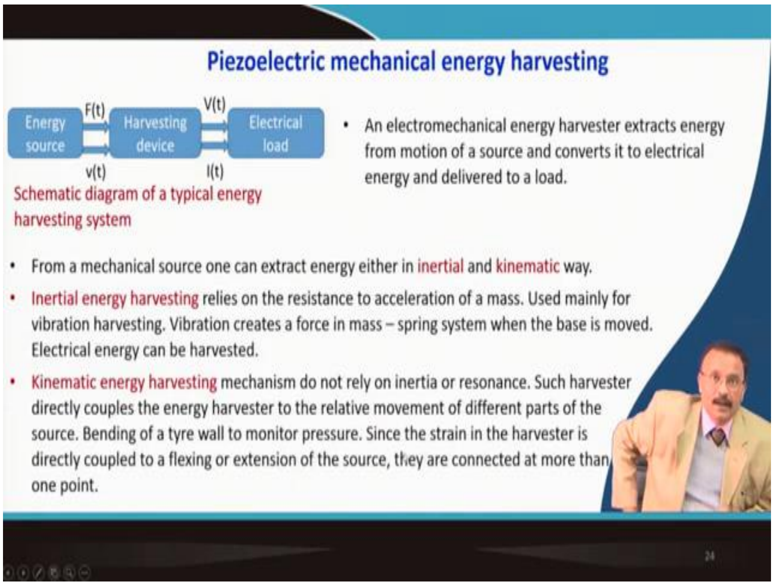

Piezoelectric mechanical energy harvesting

Schematic diagram of a typical energy harvesting system

- An electromechanical energy harvester extracts energy from motion of a source and converts it to electrical energy and delivered to a load.

- From a mechanical source one can extract energy either in inertial and kinematic way.
- Inertial energy harvesting relies on the resistance to acceleration of a mass. Used mainly for vibration harvesting. Vibration creates a force in mass – spring system when the base is moved. Electrical energy can be harvested.
- Kinematic energy harvesting mechanism do not rely on inertia or resonance. Such harvester directly couples the energy harvester to the relative movement of different parts of the source. Bending of a tyre wall to monitor pressure. Since the strain in the harvester is directly coupled to a flexing or extension of the source, they are connected at more than one point.

Finally we will introduce the piezoelectric base mechanical energy harvesting schemes and you know that when the piezoelectric material acts like a transducer. So, when something is vibrating, it can generate voltage out of it. So, the scheme of electron mechanical energy harvester extracts the energy from a motion of a source that converts it to electrical energy when it is delivered to a load.

So, from a mechanical source, one can extract energy either by inertia or by a kinematic way. So, in case of inertial energy harvesting, that relies on the resistance to resistance to the acceleration of a mass. So, used mainly for vibration harvesting. So, vibration creates a force in mass and a spring system when the base is moved.

So, electrical energy can be harvested. The second one is kinematic energy harvesting, they do not rely on this kind of inertia or resonance. So, this kind of harvested is directly coupled couple the energy harvested to the relative movement of different parts of a source, some kind of source.

So, for example, bending of a tire wall to monitor the pressure. So, the strain in the harvester is directly coupled to a flexing or extension of the source, they can they are they can be connected in multiple numbers. So, not only in one point, in multiple points they can be connected to harvest the energy.

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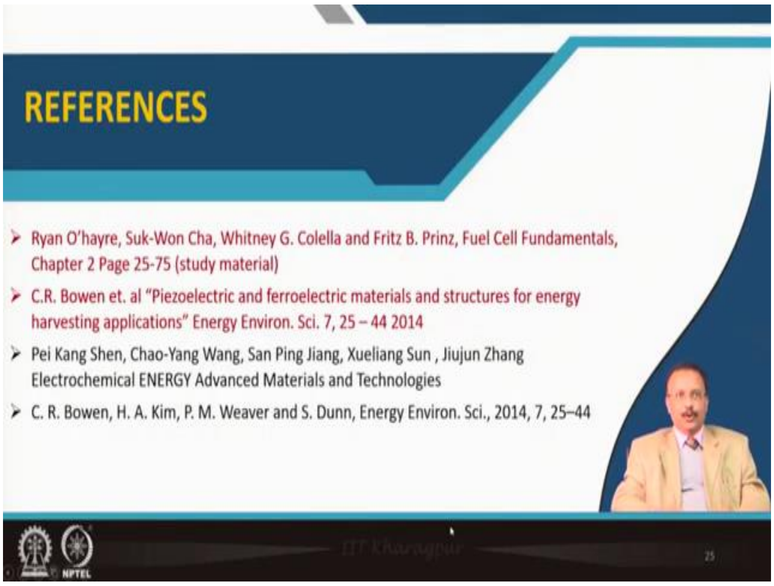

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So, the study material for this is given in these two books and as well as certain paper also I have, I am recommending for this study material for this part of the course.

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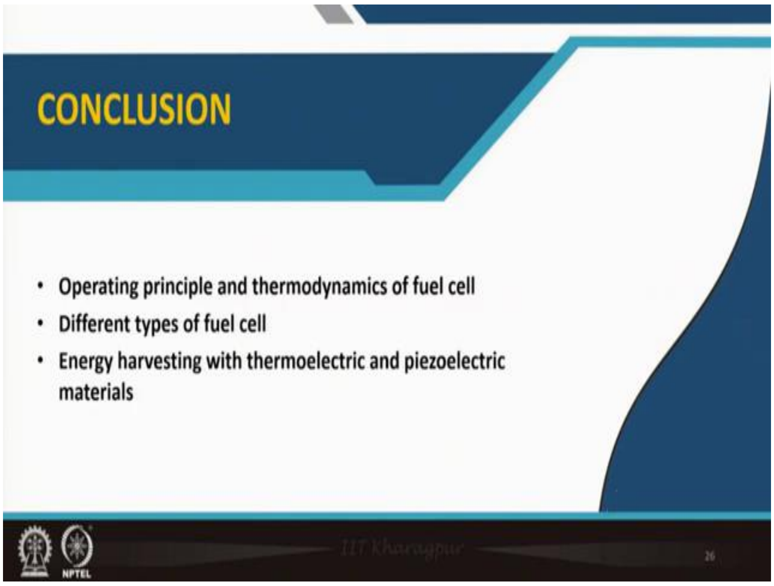

CONCLUSION

- Operating principle and thermodynamics of fuel cell
- Different types of fuel cell
- Energy harvesting with thermoelectric and piezoelectric materials

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And in this course, in this particular lecture, we have introduced the operating principle and the thermodynamics of fuel cells. And eventually we have described different types of fuel cell and just we have introduced the energy harvesting is possible by using thermoelectric and piezoelectric material.

Thank you for your attention.