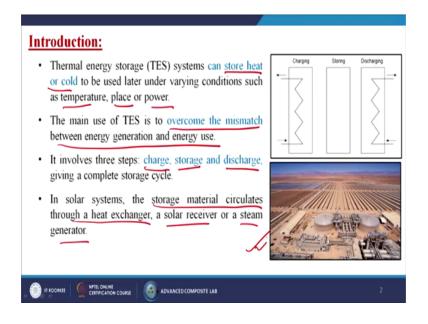
## Selection of Nanomaterials for Energy Harvesting and Storage Application Prof. Kaushik Pal Department of Mechanical and Industrial Engineering Indian Institute of Technology, Roorkee

# Lecture – 20 Thermal Energy Storage

Hello my friends, today we are going to discuss about the lecture number 20; Thermal Energy Storage which is the last lecture of this particular subjects. So, basically this lecture has been divided into two parts; the first part we are going to discuss about the thermal energy storage.

And in the second part we are going to discuss about the overview of the whole subject that is Selection of Nanomaterials for Energy Harvesting and Storage Applications, so that we can recognize that from first lecture 20th lecture what we have done and it will give a one kind of remember to that whole particular subject.

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So, now let us start with the introductions; so basically if I talk about the thermal energy storage. So, basically from the name itself we can understand that basically we are dealing with some kind of temperature or may be the heat. So, thermal energy storage in short basically we are calling it as TES systems can store heat or cold; so basically this is the things over there.

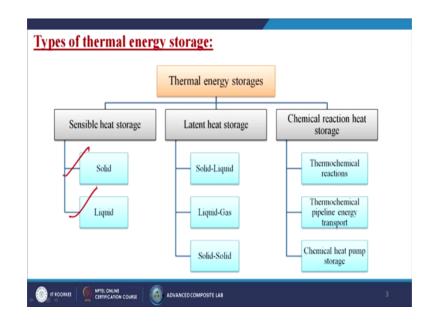
So, in this particular case; so what we are going to do? Just we are storing the heat or maybe the cold means anyway either it is hot or maybe the cold, we are storing the heat and cold to be used later under wearing conditions; such as temperature place or maybe the power. The main use of TES is to overcome the mismatch between energy generation and the energy use.

So, in this case what is going on? See, suppose I am having on materials, I am charging it and then I am storing that particular energy into some systems. And then when and where I need that particular energy just I am taking it out; that means, I am discharging the energy from that system. It involves three steps charge, storage and discharge giving a complete storage cycle.

Say, suppose battery; so initial stage what I am doing? So, battery first initial stage I am storing the charge over there; that means, I am charging that battery then I can take that battery where is my applications to the application place itself. That means, I am storing the energy inside it and now I am moving the battery from one place to another and then as and when required just I am discharging it. So, same thing; so when a new battery we are purchasing from the shop; that means, it is coming from some company; so, that company is charging that battery.

Now, the storage systems has come to the shop, so we are taking it from there and then after that we are using that particular battery; that means, we are doing the discharging over there. In solar system, the storage material circulates through a heat exchanger, a solar receiver or a steam generator. So, this is the full overview basically of a thermal storage system plant. Now, let us discuss about the types of thermal energy storage.

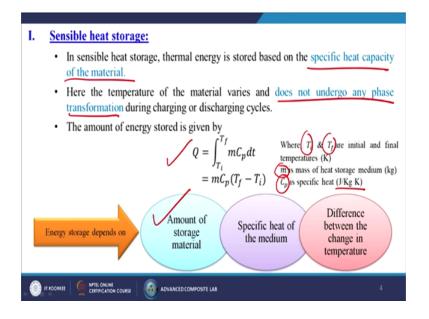
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So, basically the thermal energy storage has been divided into three parts; one is called the sensible heat storage under which the solid or liquid material can work. Then latent heat storage, either it is a combination of solid liquid or maybe the liquid gas or maybe the solid solid. And the third one is called the chemical reaction heat storage which is the thermo chemical reactions or may be thermo chemical pipeline energy transport or maybe the chemical heat pump storage.

So, basically this is the overall types of thermal energy storage; now what do we mean by sensible heat storage?

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In sensible heat storage, thermal energy stored based on the specific heat capacity of that material. So, whatever the materials we are going to choose that material should have high specific heat capacity; that is the prime requirement for any kind of material; what material we are going to use for sensible heat storage system.

Here the temperature of the material varies and does not undergo any phase transformation during charging or discharging cycle. Say, I can give you one example like stainless steel say; suppose stainless steel at 723 degree centigrade; it is having one phase. If I raise the temperature up to 900 or maybe 930 degree centigrade; it can transform to other phase; that material should not be acceptable in this particular stage because when I am heating that particular materials, it should not change.

Because when the phase change will be taking place; the whole material physical properties is going to be changed. Suppose in one phase the material is having a very good thermal resistance property or maybe the wear resistant property. Then when I am changing the temperature, it is going to the another phase; so basically that time the material physical properties will change; either the thermal properties will change or may be wear coefficient can be changed.

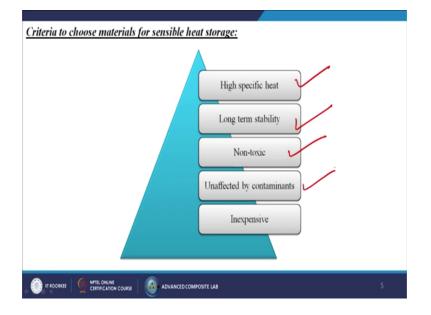
So, this should be discarded in this particular case. Now what is the amount of energy stored? That has been given by this particular equations that is capital Q is equal to integral T i to T f; m C p d t. So, where T i and T f are the initial and final temperature.

So, I do not know that what is T i and what is the T f; may be the difference is too much in between T i and T f.

So, that is why I am telling in between T i and T f; material should not change its phase. Now m is the mass of heat storage medium and C p is nothing, but the specific heat that is Joule per kg Kelvin. So, now energy storage depends on amount of storage materials because it directly depends upon m value. Specific heat of the material or maybe the medium, that is called the C p and difference between the change in temperature which is nothing, but the T i and the T f; that means, initial temperature and the final temperature.

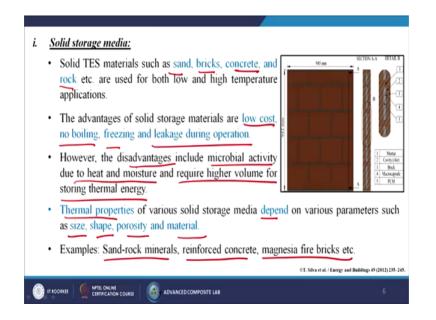
Now, criteria to choose the material for sensible heat storage; that means, what should be the material properties based on that we can choose the material for these particular thermal energy storage systems.

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So, like the material should have high specific heat, long term stability, nontoxic because I am changing the temperature; it should not produce any kind of gases over there. Unaffected by contaminants; that means, it should not react with some kind of doping materials or maybe impurities and it should be very very cheap.

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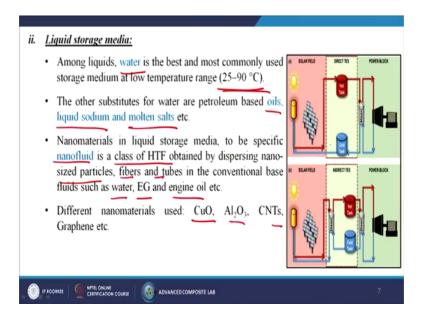


Now, it has been divided into two parts as I told already; so first one is called the solid storage media. So, solid TES materials such as sand, bricks, concrete and rock are used for both low and high temperature applications. The advantages of solid storage materials are low cost, no boiling point; that means, of course, it is having some boiling point or maybe without boiling, but the boiling temperature is too high and before that our T f should be finished.

Then, freezing and leakage during operations; however, the disadvantages include microbial activity due to heat and moisture and require higher volume for storing thermal energy; that means, m mass should be into the higher scale. Thermal properties of various solid storage media depend on various parameter such as size, shape, porosity and the material; next examples like sand-rock materials, reinforced concretes, magnesia, fire bricks; so these all are the examples.

Next is called the liquid storage media; that means, here we are going to use some kind of liquid materials. And nowadays you can see that we are adding so many nano fillers or maybe the nano materials with that liquid or sometimes we are calling it as a nano fluid also; they are having a very high absorbing capability so that the high temperature can move from one place to another.

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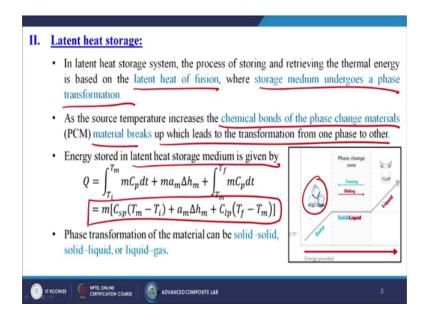
So, among liquids; water is the best and most commonly used storage medium at low temperature. Yes because the water boiling point is 100 degree centigrade; so, the range is around 25 to 90 degree centigrade. The other substitutes for water are petroleum based oils, liquid sodium and the molten salts, but the problem is that maybe some petroleum products can generate the toxic gases at high temperature.

Nano materials in liquid storage media to be specific nanofluid; as I told already nanofluid is nothing, but the nanofiller reinforced fluid. The fluid itself is not into the nanoscale; fluid is fluid, but we are adding certain kind of nanofillers over there; is a class of HTF obtained by dispersing nanosized particles, fibers, tubes in the conventional base fluids such as water, ethylene glycol or maybe the engine oil. Different nano materials, as I told already basically we are adding copper oxides, alumina 1 2 O 3, carbon nanotubes, graphene etcetera so that the heat storing capability will be increased in that particular liquid system.

So, simple we are having that sunlight, we are capturing that sunlight then we are heating the water; the water is passing through the hot tank and then I am having the another cold tank which water is not heating; it is exchanging the heat from the hot water to the cold water and due to that you are rotating the turbine over there. So, basically what is happening? From high temperature water to low temperature the heat will be dissipated very fast. So, during that heat flow that is we are capturing that heat; which is rotating

your turbine or maybe generating the high steam over there due to that the turbine is rotating. And then the generator is coupled with that particular turbine and we are generating the electricity or maybe the storing the electricity over there or maybe we can absorb that high temperature over there and that as a thermal energy we can store it over there. So, anything we can do from this particular technology.

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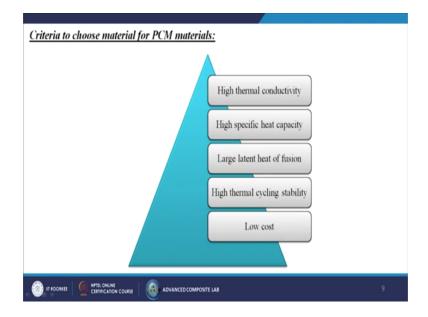
Next, the second one is called the latent heat storage; in latent heat storage system the process of storing and retrieving the thermal energy is best on the latent heat of fusion; where storage medium undergoes a phase transformations.

Now, I need certain materials which will change its characteristics in between that. The best example is water because we know that when you are freezing the water; it is into the solid that is the ice. When we are just into the room temperature; it is into the liquid phase and then we are; when we are raising the temperature it is going into the gaseous stage; that means, at different temperature; the water behaves differently one place it is solid, one place it is liquid, one place it is gas.

As the source temperature increases, the chemical bonds of the phase change materials breaks up which leads to transformation from one phase to another. So, what is happening? So, solid that is having a perfect crystal structure over there, but when it is liquid; there is no crystal structure. So, when it is going to the gas phase; so atoms are freely randomly moved over there. So, like this way simple we are storing the energy inside the system.

So, energy stored in latent heat storage medium is given by capital Q is equal to T i to T m, integration of T i to T m m C p d t plus m; a m del h m plus integral of T m to T f m C p d t. So, if we solve this problem then we will get the final equations is this one, where the m is the mass of that material itself; T i and T m is the initial temperature and the melting temperature and T m is nothing, but the final temperature over there. So, phase transformation of materials can be solid-solid, solid liquid or maybe the liquid gas combination.

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Now, criteria to choose materials for PCM materials; like high thermal conductivity, high specific heat capacity, large latent heat of fusion, high thermal cycling stability and of course, the it should be very very inexpensive in nature. Now the latent heat storage materials also have been divided into three parts; one is called the organic materials, then inorganic materials, another is called the eutectics materials.

So, if we see into the organic materials; it has been also divided into two parts one is called the paraffin or maybe the wax based, another one is called that non paraffin based.

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Latent heat storage materials cla	ssification:	
L	atent heat storage materials	
Organic	Inorganic	Eutectics
Paraffin	Metallic	Inorganic-Inorganic
/ Non-Paraffin	Salt hydrates	Organic-Organic
		Inorganic-Organic
	ADVANCED COMPOSITE LAB	10

If we talk about the inorganic that is also the metallic and salt hydrates materials. And when we are talking about the eutectics; it has been the inorganic inorganic combinations or maybe the organic organic combinations or maybe the organic inorganic combinations.

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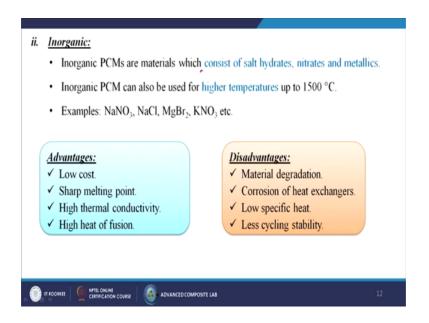
i.	<u>Organic:</u>		
	A phase change material which contains carbon atom is known as organic PCM.		
	<ul> <li>It is classified into paraffin and non-paraffin.</li> </ul>		
	- Organic PCMs are available for a wide range of temperatures which are stable till 300 $^{\circ}\mathrm{C}.$		
	• Examples: Wax, Hydroquinone, salicylic acid, alpha glucose, acetamide etc.		
	<ul> <li>Nanomaterials used in paraffin: Carbon nanofibers, CuO, Fe<sub>3</sub>O<sub>4</sub>.</li> </ul>		
	( d. downstream)	Dirahantaan	
	<u>Advantages:</u>	Disadvantages:	
	✓ Chemically stable.	✓ Low thermal conductivity.	
	✓ High heat of fusion.	✓ Mildly corrosive.	
	✓ No tendency of supercooling.	✓ High cost.	
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Now, what is organic? A phase change materials which contains carbon atom is known as organic PCM. It is classified into paraffin and the non paraffin materials organic PCM's are available for a wide range of temperatures which are stable till 300 degree

centigrade; after that which starts boiling or maybe the melting. Examples wax hydroquinone, salicylic acid, alpha glucose, acetamide etcetera are the examples.

Nanomaterials also we are using like carbon nanofibers, copper oxide, Fe 3 O 4, ferric oxides; so basically these all are the materials we are going to use. Now, what is the advantages of using these kind of materials or maybe the; this technology? Because these kind of materials are chemically stable; it is having a high heat of fusions and no tendency of super cooling. So, these all are the advantage, but of course, it is having certain kind of disadvantages also; what are those? It is having very low thermal conductivity, mild corrosive in nature and the material cost is too high.

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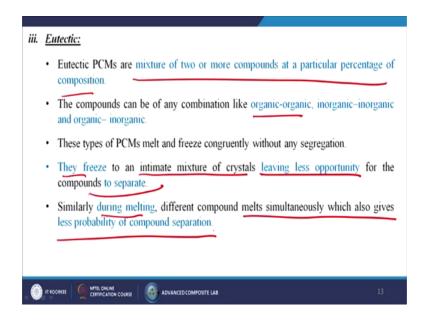
Next, we are going to discuss about the inorganic type of materials; inorganics PCM's are the materials which consists of salt hydrates, nitrates and the metallics. Inorganic PCM can also be used for higher temperature up to 1500 degree centigrade; so that is the added advantage.

In the organic case, maximum we are going to up to 300 degree centigrades, for inorganic we are going almost five times higher. So, examples is sodium nitrate, sodium chloride, magnesium bromide, potassium nitrate; so these all are the material examples. Of course, it is having some advantages what are those? The material is low cost material; it is having a very sharp melting point; that means, the melting point if is 100

degree or maybe 200 degree or 1500 degrees temperature; so, exactly that time the melting starts.

Next, the third one is high thermal conductivity and last one is that high heat of fusion. So, these all are the advantage, but of course, this material is also having certain disadvantages that material degradation takes place within that particular temperature range, corrosion of the heat exchanger maybe they are generating certain kind of toxic gas which can react with the heat exchanger materials and do some kind of corrosions. Low specific heat and less cycling stability; that means, we cannot use that particular material for so many times, that may be the drawback of these particular materials.

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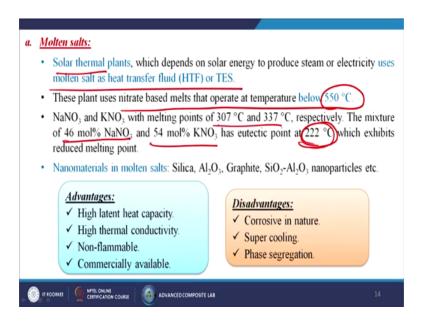


Now, what is the eutectic? Eutectic PCM's are mixture of two or more compounds at a particular percentage of compositions. So, basically this is certain kind of composite kind of materials basically. So, the compounds can be of any combination like organic-organic, inorganic-inorganic or maybe the organic and inorganic combinations.

These types of PCM's melt and freeze congruently without any segregation; so that means, when I am mixing the organic inorganic materials so, whether we are going to heat it or maybe we are going to cool it; the material will not be segregated, they will behave like a single material. They freeze to an intimate mixture of crystals leaving less opportunity for the compounds to separate.

Similarly, during melting different compounds melt simultaneously which also gives less probability of compound separation; that means, if I am adding two materials; though both the materials is having different melting temperature and different freezing temperature but when I am going to join these both material; after that it will behave like a single material having a single melting temperature and a single freezing temperature.

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Now, come to the molten salts that what kind of molten salt basically we are using. In the solar thermal plants which depends on solar energy to produce steam or electricity uses molten salt as heat transfer fluids or maybe the TES. This plant uses nitrate based melts that operate at temperature below 550 degree centigrade. Sodium nitrate and potassium nitrate with melting point of 307 degree centigrade and 337 degree centigrade respectively; the mixture of forty six percent mole NaNO 3 and 54 percent mole KNO 3 has eutectic point at 222 degree centigrade which exhibits reduced melting point.

Now, both the material is having different melting point you see, but when I am mixing that 46 percent and 54 percent together; then after that they are showing only a single melting point over there that has been reduced. So, nanomaterials in molten salts like silica Al 2 O 3, graphite and silicon dioxide Al 2 O 3 combinations nanoparticles basically we are using. Of course, these materials is having certain advantages; so, like it is having high latent heat capacity, high thermal conductivity, nonflammable and commercially available.

Of course, these materials is having certain disadvantages too; it is corrosive in nature, it is super cooling problem and the phase segregation may takes place. But it all depends upon the what kind of materials; that means, what kind of fillers or the liquids or maybe what kind of salts we are going to use.

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III. <u>Chemical reaction heat storage:</u>		
<ul> <li>Energy can be stored in a chemical reaction, which can occur in both forward and reverse directions.</li> <li>Endothermic energy can be used to form a product.</li> </ul>		
• Energy stored in a product can be regained by exothermic reaction under specific conditions.		
Thermochemical energy can be roughly presented as the following sequence.		
1. During charging $A + B + thermal energy \rightarrow C + D$		
2. Reactants can store thermal energy for long duration		
3. During discharging $C + D \rightarrow A + B + thermal energy$		
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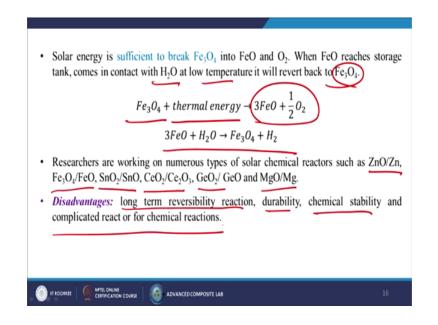
Next third one is called the chemical reaction heat storage. So, energy can be stored in a chemical reactions; which can occur in both forward and reversed direction. So, simple I am adding two materials at the time of adding that materials maybe it is exothermic reactions; so it can generate the heat over there and then automatically the byproduct will come.

Or maybe it can be with the endothermic reactions also; it can absorb the temperature; so this is the vice versa case kind of things. So, endothermic energy can be used to form a product, energy stored in a product can be regained by exothermic reaction under specific conditions. Thermo chemical energy can be roughly presented as the following sequence; during charging A plus B; if I give the thermal energy over there, then only it can produce C plus D.

Now, just I want to make it opposite I am having the C plus D; so when I will add C plus D; automatically it will release the thermal energy over there. So, like this way we can store the thermal energy inside the system. Reactants can store thermal energy for long

durations; during discharging C plus D tends to A plus B plus thermal energy; so now we can collect this thermal energy in future.

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Solar energy is sufficient to break Fe 3; O 4 into Fe O and oxygen; when Fe O reaches storage tank comes in contact with H 2 O water at low temperature; it will revert back to Fe 3 O 4; that means, it is a continuous recycling process.

Now, Fe 3 O 4 plus thermal energy which is coming from the solar itself; so by reaction it is making 3 Fe O plus half oxygen; so 3 Fe O plus H 2 O; it will convert into Fe 3 O 4 plus hydrogen. Researchers are working on numerous types of solar chemical reactors such as zinc oxide zinc; Fe 3 O 4 Fe O, Sn O 2, SN O, C e O 2; Ce O 3, then G; germanium oxides Ge O 2; Ge O combinations or maybe the magnesium oxide magnesium combinations.

Of course, these materials has been certain disadvantages, long term reversibility reactions, durability, chemical stability and complicated react or for chemical reactions; so this maybe happen.

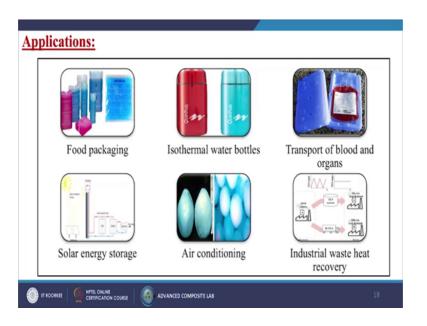
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Advantages of TES:		
✓ Helps to cut down electricity bill.		
✓ Facilitates effective utilization of intermittent renewable sources.		
✓ Environmental impact is reduced.		
✓ Reduces need for increased peak generation capacity.		
<ul> <li>Disadvantages of TES:</li> <li>✓ Additional cost and complexity.</li> <li>✓ Additional infrastructure and space requirements.</li> </ul>		

Now, what are the advantages of TES? Helps to cut down electricity bill, facilitates effective utilization of intermittent renewable sources. So, what is happening? We are not going to give any kind of energy to this particular system; only I am having that two materials and I am doing certain kind of chemical reaction over there.

Environmental impacts is reduced; reduces need for increased peak generation capacity; of course, this material is having certain disadvantages also. It is having some additional cost and complexity, additional infrastructure and space requirements are highly required; where we are applying this kind of technology?

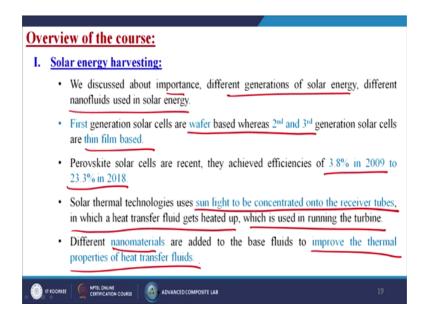
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So, generally for the food packaging, isothermal water bottles, transport of blood and organs, solar energy storage, air conditioning and the industrial waste heat recovery; so these all are the places basically we are using this particular technology. Now, let us come to the second part of this particular lecture just where we are going to provide you the glimpse that what we have covered from our 1st lecture to the 20th lecture.

So, in this particular lecture basically we have discussing into two parts; one is called the energy harvesting, just the generation of the energy and then storing of that particular energy; so it has been divided into two parts. So, and the point of harvesting systems we has first discussed with the solar energy harvesting.

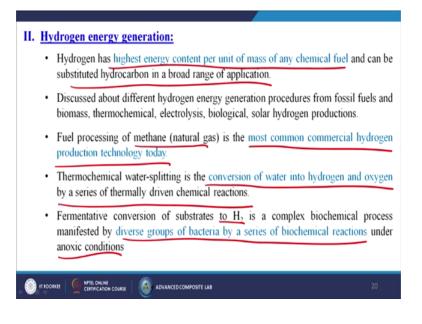
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So, we discussed about importance, different generations of solar energy, different nanofluids used in the solar energy. First generation solar cells are wafer based where are second and third generation solar cells are thin film based. Perovskite solar cells are recent; they achieved efficiencies of 3.8 percent in 2009 to 23.3 percent in 2018; so, within 9 years; they have reached almost 20 percent extra.

Solar thermal technologies uses sunlight to be concentrated on to the receiver tubes in which a heat transfer fluid gets heated up; which is used in running the turbine. Different nanomaterials are added to the base fluids to improve the thermal properties of heat transfer fluids. So, basically this is will give you a brief summary of that solar energy harvesting system. Next, we have discussed about the hydrogen energy generation.

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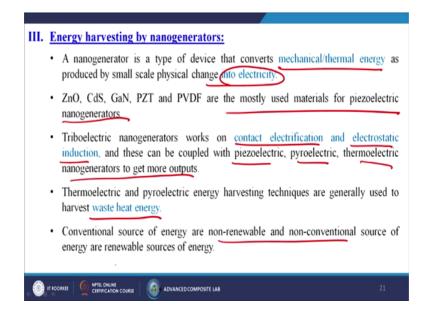


So, hydrogen has highest energy content power unit of mass of any chemical fuel and can be substituted hydrocarbon in a broad range of applications, discussed about different hydrogen energy generation procedures from fossil fuels and biomass, thermochemical, electrolysis, biological, solar hydrogen productions.

Fuel processing of methane like natural gas is the most common commercial hydrogen production technology today. Thermo chemical water splitting is the conversion of water into hydrogen and oxygen by a series of thermally driven chemical reactions. Fermentative conversion of substrate to hydrogen is a complex biochemical process manifested by diverse groups of bacteria by a series of biochemical reactions under anoxic condition.

So, basically we have discussed all these things in that particular hydrogen energy generation part. Next we have discussed about the energy harvesting by nano generators.

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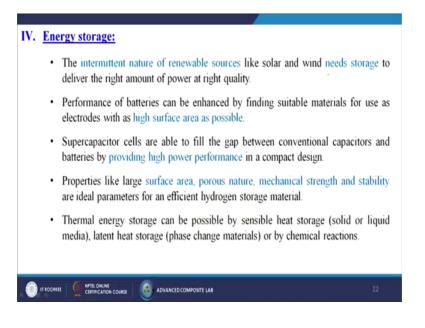


A nanogenerator is a type of device that converts mechanical or maybe the thermal energy as produced by small scale physical change into electricity. Zinc oxide, cadmium sulfide, gallium nitride, PZT; piezoelectric materials and the PVDF; polyvinylidene difluoride are the mostly used materials for piezoelectric nanogenerators.

Triboelectric nanogenerators which is based on the frictions because tribo; that means, frictions works on contact electrifications and the electrostatic induction. And this can be coupled with piezoelectric, pyroelectric, thermoelectric nanogenerators to get more outputs; that means, it is certain kind of hybrid kind of nanogenerators. Thermoelectric and pyroelectric energy harvesting techniques are generally used to harvest waste heat energy. Conventional source of energy are non renewable and non conventional source of energy are renewable source of energy.

So, we have discussed all these things in that particular energy harvesting by the nanogenerator part. Next, we have discussed about the energy storage systems; now have generated the energy, now we are going to store that particular energy how to do that?

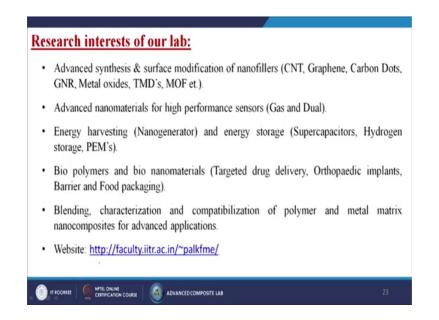
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The intermittent nature of renewable sources like solar and wind needs storage to deliver the right amount of power at right quality. Performance of batteries can be enhanced by finding suitable materials for use as electrodes with as high surface area as possible. Super capacitor cells are able to fill the gap between conventional capacitors and batteries by providing high power performance in a compact design.

Properties like large surface area, porous nature, mechanical strength and stability are ideal parameters; for an efficient hydrogen storage materials. Because the gas can be stored inside the porous materials, it can make a trap kind of things. Thermal energy storage can be possible by sensible heat storage solid or liquid media, latent heat storage, phase change material or by the chemical reactions which we have discussed the first part of this particular lecture.

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Now, I am going to discuss little bit about our lab. So, basically in our lab we are working as a whole group and the whole group are working into different applications. Basically, we are working on the energy storage device, energy generation device, we are working on the sensors, we are working on the biomaterials, we are working on the biopolymers, we are working on the materials for orthopedic implants.

We are working for the materials for the aerospace industry, but basically our main specialization is that to synthesize the different types of nanofillers, modifying those nanofillers or making some kind of new composite systems; which can sustain into all those applications. So, at the onset we are working on the advanced synthesis and surface modifications of nanofillers; like we are working on carbon nanotubes, graphene already we have made the graphene and we have derived certain kind of new technology; which is called the improved Hummer's method that by which we are making the reduced graphene oxides.

We are working on the carbon dots, we are working on the gold nanorods, gold nanoparticles; we are using on the graphene nanoribbons metal oxides basically we are using; we are using on the transition metal dichalcogenides and nowadays also we are working on the metal organic framework. Also we are working on the advanced nanomaterials for the high performance sensors; basically we are working on the dual gas sensor, humidity sensor and the some kind of toxic gas sensors. We are working on

the energy harvesting system; that is best basically on the nano generators and energy storage systems, basically we are working on the flowable super capacitor, hydrogen storage systems, polymer electrolyte membranes. And also another part we are working on the bio polymers and the bio nanomaterials; basically we are dealing with the targeted drug delivery for the breast cancer and for basically for the lung cancer.

We are working on the orthopedic implants basically we are using the magnesium alloy for making any kind of knee joint or maybe the hip joint, we are working on the barrier and the food packaging systems. So, basically we can keep the food for a longer time and overall basically we are working on the blending characterizations and compatibilization of polymer and metal matrix nanomaterials for the advanced applications. We did certain work on the aerospace applications that for the aluminium metal matrix composites.

We did work certain kind of polymeric nanocomposites, basically for the automotive parts like car bumpers or maybe that, car bonnet systems. So, basically this is the website; where you can get the information's about our lab and actually what we are doing and also you can get certain kind of publications details over there and it will give you whole summary of our particular lab.

So, this is basically the group members. So, as a team basically we are working all together; so there is nothing like any hierarchy over there. So, being a team member basically we are working. So, now our group consists almost like 14 to 15 people. So, basically we are working together and we are trying to do this kind of research.

Thank you very much for your patience.