Electrochemical Energy Storage
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Module - 11
Li resources and recycling of Li ion batteries
Lecture - 54
Recycling of Lithium and other Battery Constituents from Used Battery

Welcome to my course Electrochemical Energy Storage and we are now in Module number 11, Lithium resources and recycling of Lithium ion batteries and this is Lecture number 54, where we will describe the Recycling of Lithium ion and other Battery Constituents from the Used Battery, which is very important aspect to talk about.

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And first I will describe the trend of lithium ion battery research and then what we called end of life vehicle management. So, this is the graveyard of electric vehicles in recent times in china and you can see that how many vehicles are abundant and all this contain lithium batteries a sizeable amount of lithium is used in this making this EV batteries. So, we will have to extract it and we have limited lithium resources which very important to understand and know that how they are exactly done as far as the current technology goes.

Reverse chain supply of lithium ion battery how you will get it back from the actual user back to the recycler so that is important. Then we will talk about basic recycling processes and global lithium ion battery market and in that context why lithium recycling is important? And what are the present consumptions and who are the prominent recycle recyclers. So, this will be covered in this course in this particular lecture.

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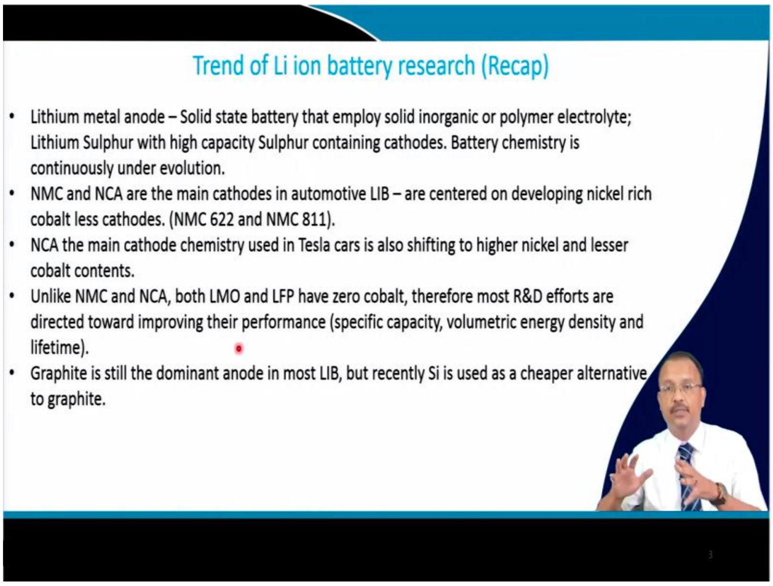

So, let us have a look of the trend of lithium ion battery research and this is mostly a recap already we have talked about it. Lithium metal anodes it is solid state battery that employ solid inorganic or polymer electrolyte. So, lithium metal anode that is in lithium polymer batteries that is one they directly use the lithium metal foils.

Lithium sulphur which is a future technology that is due to the high capacity sulphur containing cathodes already I have covered this topic in one of the modules of this course. And battery chemistry is currently under constant evolution. So, better chemistry will come and more use of lithium can be predicted as compared to whatever you have in the present days batteries.

This nickel manganese cobalt base NMC and aluminium doped nickel cobalt they are remain the main cathodes for automotive LIB and nickel rich and cobalt less cathode they are the technology trend. So, as you can see here the nickel content is quite high this 622 batteries and 811 batteries it is still higher and nickel will increase the nominal voltage of the battery as well and cobalt is expensive as well as toxic.

So, NCA is the main cathode chemistry that is used in Tesla cars and that is also shifting to higher nickel and lesser cobalt contents so the trend remain same. And NMC and NCA apart from that both lithium manganese oxide and lithium iron phosphate they have zero cobalt, they do not use any cobalt. So, most R and D efforts are directed towards improving their performance, because still there are some issues with the spinel base electrode particularly at the lower voltage limit when lithium more lithium is getting into the battery system.

Then jahn teller distortion and those kind of difficulties that is yet to be completely eliminated manganese dissolution in the electrolyte is another problem. So, people are working on specific capacity, volumetric energy density and lifetime increment or the lifetime at least should have 500 cycles it should run with the capacity fading mostly up to 85 percent.

As far as the anode is concerned graphite is still dominant anode recently silicon that is used is a cheaper alternative to graphite but there are other issues like volumetric expansion. So, that is the more or less recent trend of the battery. So, you have this cathode materials that is there in the battery which needs to be recycled.

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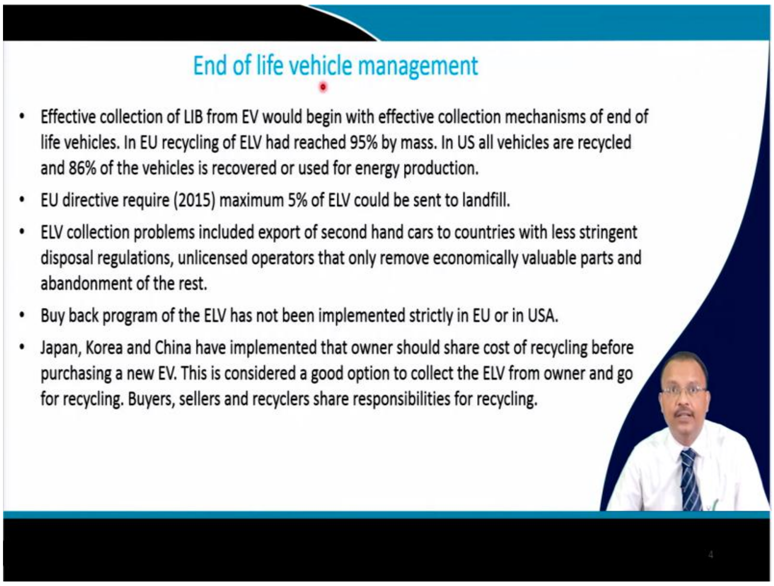

So, it is important end of life vehicle management. So, effective collection of lithium ion battery from electric vehicles that would begin with effective collection mechanism of the end of the life vehicles, which is which has already gone to the graveyard. So, in

European Union recycling of this end of life ELV vehicles end of life vehicles that has reached almost 95 percent by mass.

And in US all vehicles are recycled and 86 percent of the vehicles is recovered or used for energy production. So, whatever you are getting back again you prepare fresh cells out of it.

So, accordingly you directive which is a bit old 2015 it told that 5 percent of ELV could be sent to the landfill 95 percent will have to be recycled. And then only it will go for the landfill purpose because this use used electric vehicles, which has ended the life is ended for these vehicles.

So, this collection problems that included export of second hand cars to the countries with less stringent disposal regulations. So, not necessary that in one particular country like China they have massive this ELV, but just before their life ends it can extra export it to some other country, where these loss are not that stringent they can still run it. And then this lithium is lost to that country, they may not have any efficient kind of recycling mechanism.

So, this unlicensed operators that only remove economically valuable parts, because one day that will also be ELV in that particular second country, which using this second hand batteries. And abandon the rest because they may use iron and other parts re cycle it, but not lithium. So, that is a loss of lithium.

So, buyback program is another way for this ELV that has not implemented strictly either in European Union or USA. That has not made mandatory that you will have to the seller will have to purchase the used car if someone comes to buy a fresh EV.

Japan, Korea and China they have implemented that owner should share the cost of recycling before purchasing a new EV. So, they are charging you that you also spent your money for the recycling and this is considered a good option to collect the ELV from owner and go to go for recycling.

So, buyers, sellers and recyclers they share the responsibility and Japan is taking the lead and China is following and as I understand Korea is also doing that. So, that is one of the good mechanism to go for this kind of recycling.

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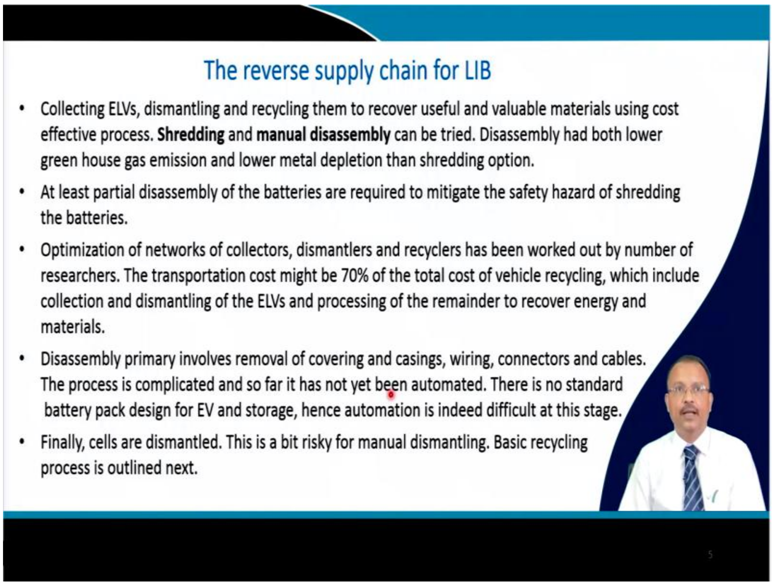

So, collecting ELV, dismantling and recycling them to recover useful and valuable material using a cost effective process that is the thrust of this kind of recycling. So, shredding can be done and manual disassembly these two things can be tried. So, if you disassemble it is having a lower green house gas emission and lower metal depletion than the shredding operation. So, but this is manually you will have to do.

So, at least one can do partial disassembly of the batteries to mitigate the safety hazard and shredding the batteries, because if it is not manually done then the battery depending of its state of charge, it can explore during shredding.

Optimization of networks of collectors, dismantlers and recyclers has been worked out by number of researchers. So, there are lot of papers available. The transportation cost might be 70 percent of the total cost of vehicle recycling. And that data is little bit alarming because most of the cost is to transport it to a proper place. And that cost include the collection and dismantling of the ELV and processing of the remainder to recover energy of the energy and materials.

So, disassembly primarily involved removal of covering and casing in the battery, then wiring, the connectors, cables, you know that what is there inside a battery pack. The process is complicated and so far has not yet been automated. So, there could be jungle of wires depending on what type of BMS you are using.

There is no standard battery pack design because you cannot automate it also the EV storage battery, they are having different types of shapes. So, automation is difficult to dismantle the battery when you are taking it out from the end of life vehicles.

Finally, the cells are dismantled. So, then you get the access of the cell in the module one get rid of BMS, thermal management system all the wirings and then you get the access of the cells and here this is a bit risky for manual dismantling. So, basic recycling process whatever is followed that I will now talk about it.

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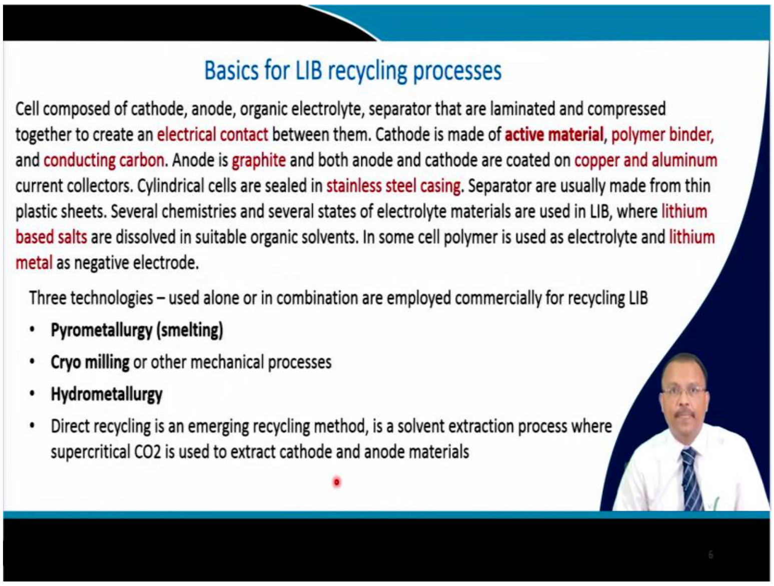

So, as you know the cell is composed of cathode, anode, organic electrolyte, separator those are laminated and compressed together to create electrical contact between them. So, cathode is basically made of active material, then you have polymer binders and conducting carbons. Anode is graphite and both anode and cathode are coated on copper and your aluminium current collector according to the current technology whatever cells you are having.

So, cylindrical cells they are sealed in stainless steel casing and separators are usually made from thin plastic sheet this cell guard 24 the polypropylene porous membrane. Several chemistries and several states of electrolyte materials are used in LIBs, where lithium based salts are dissolved in suitable organic solvent. In some case polymer is used as a electrolyte and lithium metal is used as a negative electrode material.

So, now, you can understand that what are the things that you can extract. So, metallic part is there, then in the active material you have lithium apart from that cobalt, nickel, manganese particularly cobalt, nickel and lithium can be extracted, then you have current collector, which are copper and aluminium sheet if needed you can recycle that also. Stainless steel casing is there. So, from the cell only the lithium ion cell these many things can be recycled.

So, basically there are three technologies they are used alone or in combinations these are used for the commercial recycling plant of lithium ion battery. And the first one is pyrometallurgy smelting process is involved. Then second one is cryo milling or other mechanical process at low temperature and hydro metallurgy, this is the third process.

Direct recycling is an emerging recycling method, it is a solvent extraction process where super critical carbon dioxide that is used to extract the cathode and anode materials. So, all the processes which I will describe they falls either any one of this category or in combination.

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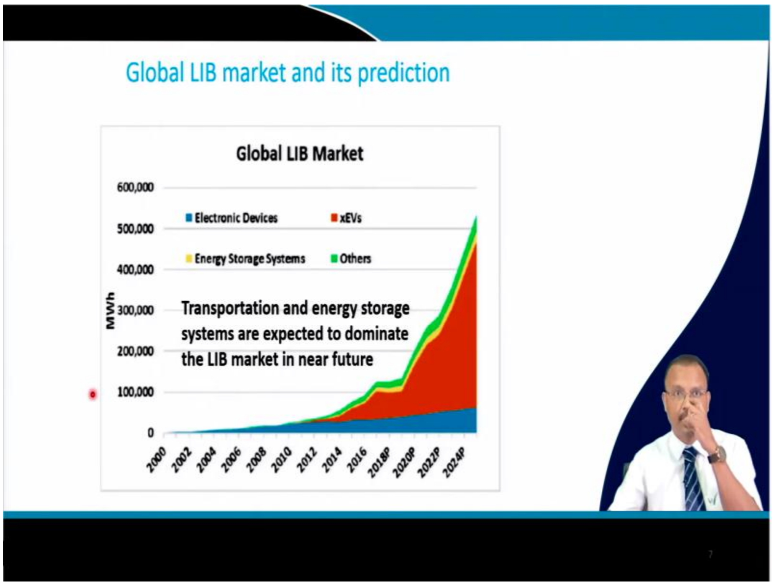

So, if you see the global market and if you note its prediction then as you can see electronic devices, this electronic devices starting from 2000 to basically till 2024 and beyond you can see there is a steady increase here. But suddenly this EV market starting from 2012 it is picking it up right and energy storage system also this is picking it up and apart from that other users this is also picking up.

So, lithium use I think will be dominated this will dominate for lithium ion battery market lithium use in LIB that will be the major use of lithium at least in near future. And other prominent source is glass ceramics making. So, that I mean it is expected that some other technology will come. So, the use of lithium will get limited and more lithium will be used in this particular purpose.

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So, it is absolutely necessary to recycle the lithium ion battery and in European Union and US they have already made it. So, you will have to recycle. Lithium batteries contains flammable and toxic components, you cannot throw it out any lithium ion battery including a computer whatever you are having you should not throw out the battery in the garbage can.

So, it is extremely dangerous disposing lithium battery for land filling because eventually it will go as a garbage for land filling it is dangerous for possible explosion can take place and contamination of the ground water that is another serious issue.

Because finally, cobalt is toxic and this will mix with the ground water. So, is it is absolutely necessary that we will have to recycle it if you use start using huge quantity of lithium ion battery and this waste management is one of the major problems nowadays whoever is using the LIB for different purposes.

India does not have lithium source. So, we import the batteries indigenous lithium battery manufacturings, that would need lithium precursor, due to this knowledge on lithium ion battery recycling is absolutely necessary. So, you take the lithium from outside and we have a huge market so many people are there. So, we will have a huge market you purchase the battery and then make that lithium resource, and start using that lithium.

So, a major part of it if you have a recycling plant here and you have the access of the battery and cells then that is also profitable and in fact, Tata motors and others they are already started working and if I understand that some recycling companies also has been established in India, I mean as of current data whatever is available.

So, the component lithium cobalt oxide the composition is about 27.5 percent, steel and nickel that is roughly about 24.5, copper and aluminium is 14.5, carbon is 16 percent and then electrolyte is 3.5 percent and polymer is 14. So, that by mass percent if you take a lithium cobalt nickel based I mean cell, then you have roughly this composition and this is a sizeable amount which can be recycled.

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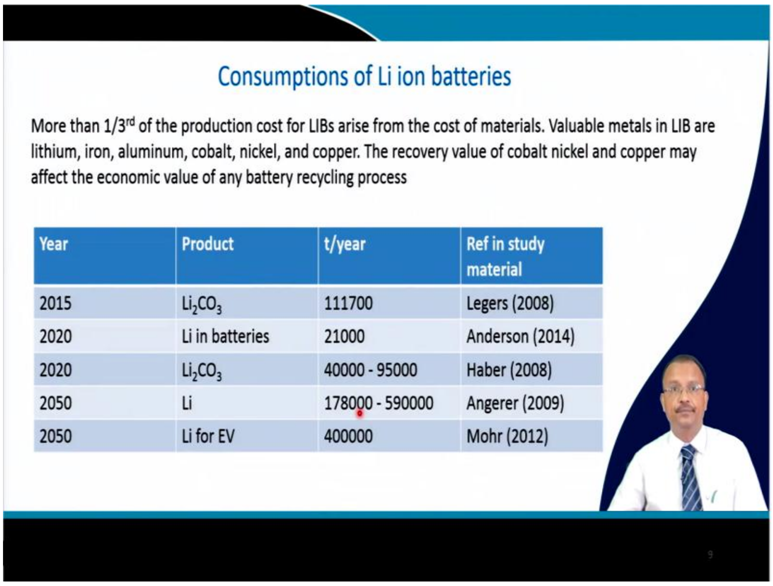

Year	Product	t/year	Ref in study material
2015	Li_2CO_3	111700	Legers (2008)
2020	Li in batteries	21000	Anderson (2014)
2020	Li_2CO_3	40000 - 95000	Haber (2008)
2050	Li	178000 - 590000	Angerer (2009)
2050	Li for EV	400000	Mohr (2012)

The consumption of lithium ion batteries you can see more one - third of the production cost of lithium ion batteries that arise from the cost of the material, so 33 percent around. Valuable metal in lithium ion batteries there are lithium, iron, aluminium, cobalt, nickel and copper you know, where from they are coming right.

So, active material contain maybe lithium iron phosphate if we use iron is there, aluminium and copper they are basically the current collector, cobalt nickel is there in the positive electrode material itself lithium comes from positive electrode material and if LTO is used lithium is there.

Recovery value of cobalt, nickel and copper may affect the economic value of any battery cycling process. So, you can see this how it will year wise will go lithium cobalt oxide sorry lithium carbonate tons per year production is this much, lithium in battery is tons per year production is this much.

Again by 2020 lithium carbonate is this much and lithium as a metal. So, this will go according to the prediction the huge amount and lithium for electric vehicles tons per year will be 400000 tons per year. So, consumption of lithium ion battery is a it will have a steady progress according to this predictive reference.

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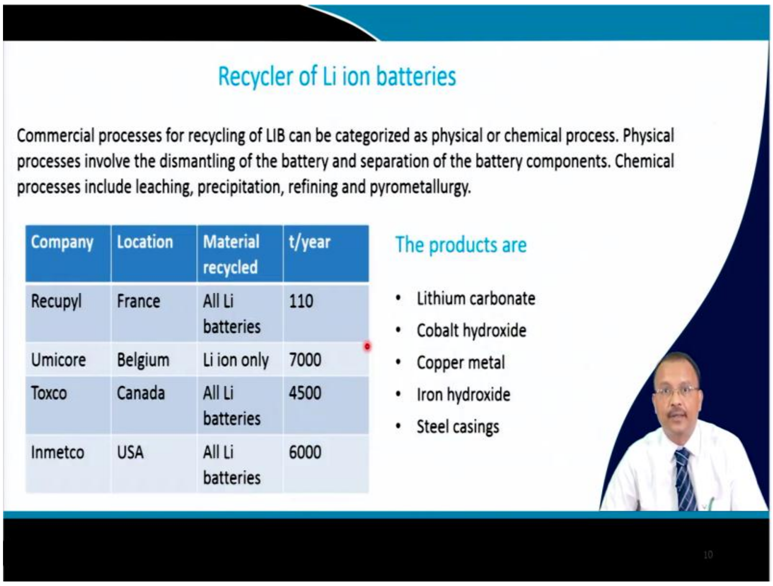

Now, commercial process of recycling of lithium ion battery, which will I will have a detailed look in my next lecture, they can be categorized as physical process or chemical process. So, the physical process they involves as I said dismantling of the battery and separation of the battery component and chemical process includes leaching, precipitation, refining, pyrometallurgy to extract the valuable component of the cell for future use.

So, the company is most there are several companies, which you can find details in the study material which I have referred at the end of this lecture. So, Recupyl, Umicore, Toxco and Inmetco. So, you can see that two of them are in Europe and Canada and USA. So, you see that all lithium batteries they recycle and this is the typical capacity 110 tons per year.

This Umicore they have the technology to extract only lithium ion, Toxco has the technology for all lithium batteries on all component of the lithium batteries and Inmetco also the capacity for all components of the lithium ion battery. So, the product that you get could be lithium carbonate recycle product, cobalt hydroxide both of them are good source for making the fresh cells, copper metal, iron hydroxide that is used in LFP and steel casings that is also reusable.

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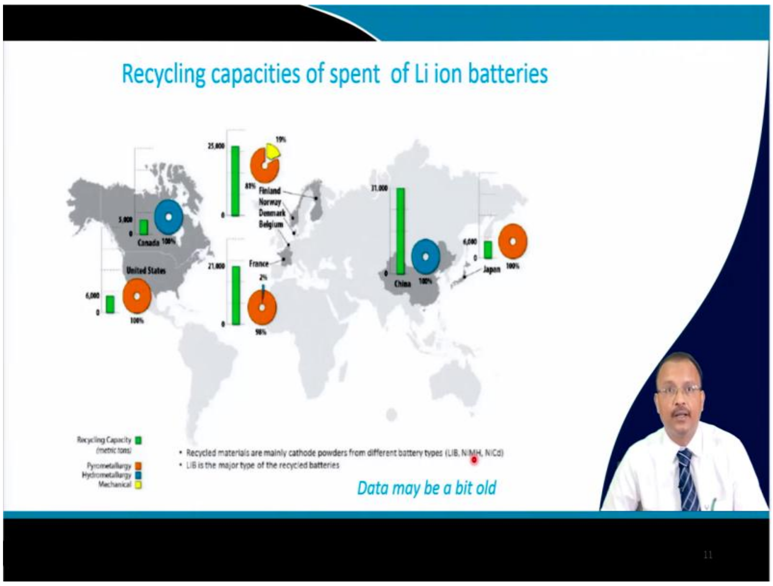

So, recycling capacity of the spent with lithium ion batteries that you can see although this font size is I am sorry for the font size is little bit smaller for you to see that, but recycling capacity that is shown in metric ton here and then this orange part, this green part is the recycling capacity total recycling capacity this green part. Then this orange part they are pyrol pyro metallurgy base basically in United States and hydro metallurgy is the blue one and the mechanical one is the yellow one which is a small part.

So, these are the region where the recycling capacity mostly in US part of Belgium, as I said and China also is having mostly by hydro metallurgy root and this data is a bit old if

I remember about 2016 data, it might have slightly changed, but these are the country this Finland, Norway, Denmark, Belgium, France, China, Japan, United States and also Canada.

Canada is also having one cycle recycling plant and also in India I believe there is one recycling part in northern part of India exactly I do not remember the factory name, but we have also started we are also into the same business.

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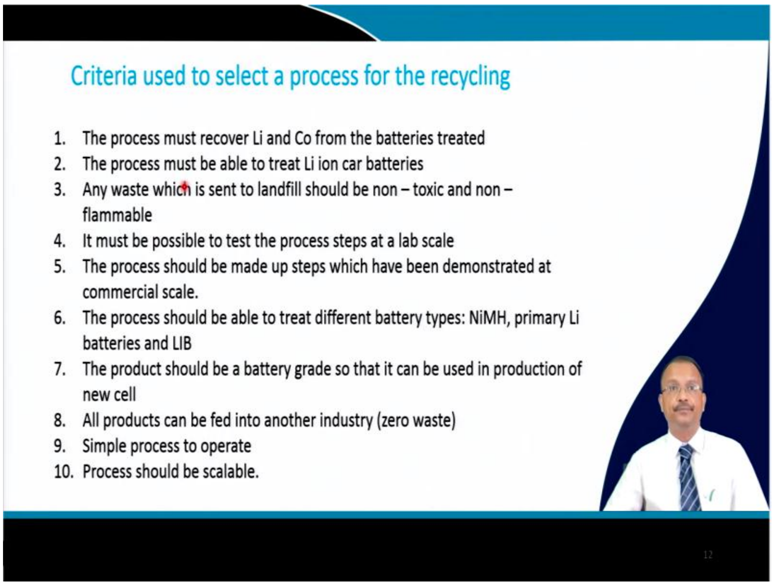

There are certain criteria that you must follow to select a process for recycling the first one is the process must recover lithium and cobalt from the battery is treated. So, some of the company they use only lithium extraction the Belgium base Umicore, but cobalt also it is mandatory. So, that also needs to be extracted recovered. The process must be able to treat lithium ion car batteries. So, not only cells, but from the battery itself the battery module as a whole should be recycled.

Any waste which is sent to landfill should not be should be actually non-toxic and non-flammable, you will have to ensure that that nothing is going out from the recycling plant. So, that that can be mixed with the ground water and contaminate the ground water. It must be possible to test the process steps at the laboratory scale. So, of course, people will do it in the laboratory scale before they have a huge plant establishment.

The process should be made up in steps, which have been demonstrated at the commercial scale this is also obvious. The process should be able to treat different types of battery because lithium metal hydride nickel metal hydride which I will be covering in my last module lecture.

So, that is also in use in for certain applications, primarily lithium batteries and lithium ion batteries so all are extractable. So, the plant should be capable ideally not all plants comply to that I am pretty sure, but ideally they should have the capability to basically recycle all this types of batteries.

The product should be a battery grade whatever you are getting out of the recycle plant and it can be used in the production of new cells. All products can be fed into another industry. So, zero waste that is a concept of zero waste whatever you are producing and whatever is the byproduct kind of thing you transfer it to the other industry for necessary extraction process. So, the waste wastage will not there you will not generate any further waste out of this process.

And this is a simple process to operate and not very complicated and process should be scalable. So, you should have at least 100 150 tons of the recycling capacity for making it profitable. So, this is the criteria roughly this 10 point criteria that is followed for the recycling.

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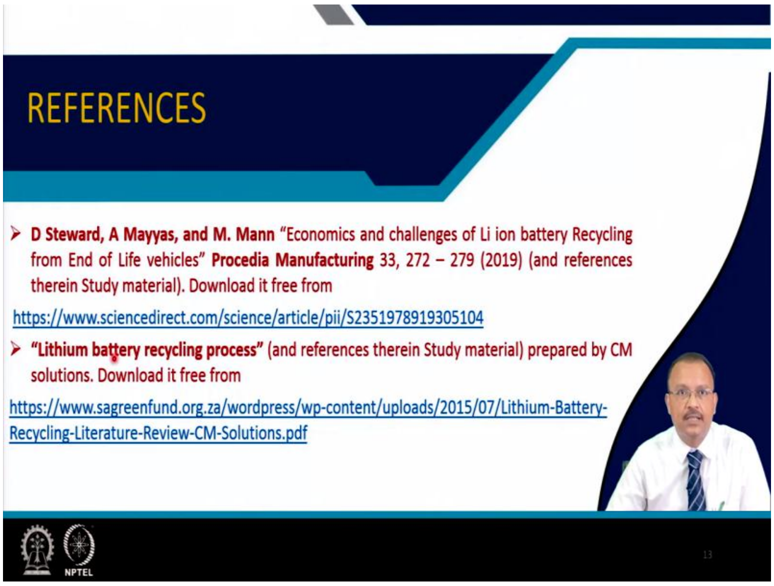

So, this paper is quite interesting and quite recent. So, you will have to download this. And this is the link for downloading this paper. And also lithium battery recycling process. So, all the references are important. So, this is actually prepared by same solutions and this is the link to download both these things and freely it is downloadable, excellent source of the concept of recycling and I have just summarize it in this lecture and I would urge you to go through this two important reference material for having more detailed idea about the concepts taught in this lecture.

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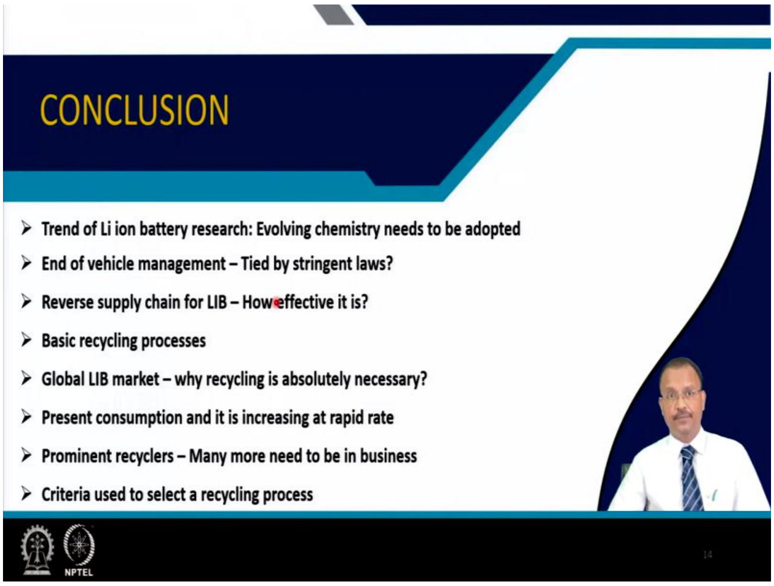

So, trend of lithium ion battery research: Evolving chemistry what is needs to be adopted for the recycling that was first described. Then end of vehicle management and this is actually tied by stringent laws, so that is there in US and European Union. Then reverse supply chain of LIB - how effective it is? Whether the battery is staying in your country or you are selling the car itself to the some other countries, who may not recycle the battery part and lithium is lost in the process and also the transition metal cations are also lost in the process.

So, this is not a good thing, what is the basic recycling process and what is a global market of lithium ion battery and why lithium ion is absolutely lithium is battery is absolutely necessary for recycling and what is the present consumption and increasing as you can see in a rapid rate. So, we have a graph of that and who are the prominent recycler and many more there are in the business. So, you will have to go through that literature, but I just referred and finally, what are the criteria's to select a particular recycling process.

Thank you for your attention.