

# **Physics of Functional Materials and Devices**

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## **Lecture – 43, Week 11**

### **Battery II**

Welcome to the first lecture of week 11. In the previous week, we had started our discussion on super capacitors, then we moved on to batteries. In the first lecture related to batteries, I talked to you about the concept of primary batteries and secondary batteries. How did we reach the concept of lithium ion batteries that was introduced? You must have seen that it took nearly 200 years from the point where voltaic pile was discovered to reach the concept and commercialization of lithium ion batteries in 1991 by Sony. And since 1991 till today itself let us say in 2023, there is a continuous development in the field of lithium ion batteries with still large improvement which is being sought by the end user in the batteries. The end user is asking the technology makers to reduce the size of the batteries while ensuring that the energy densities and the power densities are not compromised.

If you look into the batteries, you have seen that most of these batteries are charged. rigid in design, but as we move towards wearable electronics, as we move towards flexible electronics, there is a growing demand to make flexible batteries, rollable batteries and this is itself a major challenge to all of us. and we must address the wishes of the end users by making these batteries and increasing the usability of such technologies. If you want to do that you must first understand the components which are there in a typical conventional lithium ion batteries.

Why I am calling it conventional now? Because the concept of lithium ion batteries is no more new. The work started let us say around 1980s or so, or slightly before that, before it could be commercialized in 1991. does not mean that the work started in 1991 and it would immediately commercialized. There is a long duration of research activities which precede before the technology can reach the market and therefore, if you look into the time period it is already 40 years or more that the lithium ion battery is there in the market and hence

the word conventional lithium ion batteries. So, you must understand what the components are there in the conventional lithium ion batteries, how material plays important role and how the materials which you have studied till now can become useful for these technologies.

If you want to go to the next gen batteries, what would be the strategies? The ideas for this will come after you develop the understanding about this battery. In today's class therefore, I will start once again from the concept of secondary batteries. What are we meaning when we talk about advanced chemistry cells that is cells beyond lithium? I will introduce the concept about this before we end the lecture and you will see that there are various use of these batteries. based on that certain future directions of this technology will also be introduced. If you remember in the previous lecture of week 10, I had mentioned the scientist name awarded the Nobel Prize for their work in the field of lithium ion battery.

You had Professor Goodenough, Professor Whittingham and Professor Yoshino who were given Nobel Prize in 2019 for their work on lithium ion batteries and they were working on different concepts. For example, Professor Goodenough was basically working on electrodes based on lithium cobalt oxide, Professor Whittingham was also working on electrode materials, Professor Yoshino was working on non aqueous electrolytes and also on battery safety. If you see the usage of these batteries, they are being used practically everywhere nowadays from mobile phones to cameras to car batteries to certain TVs to if you look around you have your smart pens, smart boards, you have enormous applications for these batteries. These are secondary batteries that means, they are the batteries which can be recharged after a cycle of charging and discharging is over and they can be charged many times. Typical cycle life of lithium ion batteries are 1000 or more.

If I put the concept which we discussed in the previous class in the form of a graph, then you will find that if you plot the energy density in watt hour and you have energy density in watt hour / kg, then you will find that if I plot in terms of watt hour per liter, then this side means smaller size and if I move in this side you have lighter weight. So, as you see there has been the advent of various technologies. Along with that you will find that if I compare the specific energy of lead acid battery which is around 30 watt hour / kg with that of a cylindrical type lithium and battery, it has a specific capacity of 200 watt hour / kg with a corresponding energy density of 600 watt hour / liter. So, you had very different energy densities. Let us now see what is the construction and operation of a typical lithium ion battery.

You have a cathode which is based on a material for example, lithium cobalt oxide.

Lithium will leave from the lattice of lithium cobalt oxide and then it will get stored in between the layers of the graphitic type anode structure. It is the lithium ion not the electron because if the electron is moving from one electrode to the other then you will have a short circuit electronic short circuit. So, that is not possible. So, you have a lithium ion conducting electrolyte which facilitates the motion of lithium ion from the cathode to the anode during the charging cycle.

If you want to have the two sides separated so that there is no short circuiting then you also have a separator in between. So, you have a separator in between. This separator is an ion conducting membrane. That means, it will conduct ions, it will allow the flow of ions through it, but not the electrons. Which types of ions will it allow? It will allow the lithium ion to pass through and this separator membrane is soaked in the conducting electrolyte solution.

So, what will happen? When you have the charging lithium will leave the lithium cobalt oxide surface and get intercalated into the graphitic anode. So, what you will have? You will have  $\text{Li}_x\text{CoO}_2$  because certain concentration of lithium ion has moved out of the lattice of the material. So, here you will become  $\text{Li}_x\text{C}$  structure. So, lithium now goes and sits between the carbon structure during discharging. To maintain the charge neutrality condition you will have the electrons flowing from the supply and that is why you have to plug in while charging the batteries.

What will happen during discharging? The ions will move back that is lithium will move back from the anode to the cathode and when a positive charge moves back the corresponding electron will have to move out. So, that the charge neutrality condition is maintained and the flow of electron will mean what? It will mean electricity  $dq/dt$  So, you have current flowing. So, you will have the generation of electricity or flowing electricity. So, this is the discharge and when you connect the battery through an external load lithium goes back to lithium cobalt oxide and you have lithium cobalt oxide once again forming the stable lattice. This is the typical working of the lithium ion battery.

So, what are the components? You have cathode, you have electrolyte, you have anode and a separator. If you look into the same thing in a slightly enlarged manner with the separator membrane clearly shown now, which was not there in the initial Why? Because you must understand that there is a design modification from conventional batteries. There is an ion conducting membrane also between the cathode and the anode. So, if you have lithium ions then during charging lithium will move from the cathode to anode electrons will have to be supplied so as to maintain the charge neutrality conditions. Then during

discharging you will have the reverse and you will have the flow of electron and that would power your device.

This mechanism is called the rocking chair mechanism. First you see this animation and hopefully you will understand what do we mean by rocking chair mechanism. What is happening? During charging the lithium is moving out of cathode and going into anode. During discharging it is going out of anode and coming back to cathode. So, this whole mechanism appears to be like the one which you get when you are sitting on a rocking chair.

And therefore, this mechanism is called as rocking chair mechanism of lithium storage in the lithium ion batteries. Clearly, now you understand that components of lithium ion batteries or ion base batteries would be what? Would be an anode, would be a cathode, an electrolyte and a separator. You will understand the use of all of them individually. What is the anode? which is the negative electrode will drive the oxidation reaction. Oxidation reaction means it will release electrons to the external circuit during the discharging process and it has to host the incoming ions.

If you want to have the anode which has to host the incoming ions, what should be the typical nature of these structures? They should be layered structures so that ions can go and intercalate and get stored inside the structure because if you have a structure which is not layered, but solid then ions would not be able to enter the layer and you will have much smaller storage capacities. So, these layered structures should have high coulombic output, they should have relatively high conductivity. So, that they can take electron and give electron from the external circuit or to external node respectively. they should be stable why because you are impinging the larger size ions to move inside these structures and then you are extracting these ions out of this structure. So, the overall structure of the anode should be quite stable and you have various types of anode materials which are used.

Then you have the cathode which are the positive electrode you will have the reduction reactions here they will acquire electrons from the external circuit and is reduced to the original state during the discharging process. So, they are mostly efficient oxidizing agent, stable when they are in contact with electrolyte, they should be easy to fabricate, must be cost effective and then there are various types of cathode materials that are utilized. So, looking at this graph you can clearly see that you can choose the type of elements which would be useful for anode or cathode depending their ability to oxidize or reduce during the charging or discharging processes. What is an electrolyte? Electrolyte is facilitating ion transport from cathode to anode during charging and from anode to cathode back during

discharging. You have two types of electrolytes, you can have aqueous electrolytes or non aqueous electrolytes.

You can have water based electrolytes which could be acidic, alkaline or neutral. Acidic means you have  $H^+$ , alkaline you have  $OH^-$  radical and neutral means you have neither  $OH^-$  or  $H^+$  ions and then you have organic or ionic liquid paste non aqueous electrolytes. The properties of these electrolytes must be what? They should not have any electronic conductivity otherwise they would introduce short circuiting between the two electrode plates. They should be easy to fabricate, have large ionic conductivity, must not react with the electrode materials, their disposal, handling and storage must also be safe as a function of time, temperature, pressure and vibrations.

There are various types of cells which are being fabricated. They are depending upon the configuration and shape. If you have a coin type configuration, it is called a coin cell. If you have a pouch like configuration, it is called pouch cell, cylindrical cell or a prismatic cell. A typical coin cell is made up of anode, a cathode, a separator which is soaked in the electrolyte, then you have the spring which compresses the anode and the cathode so that you can ensure proper contact of these two.

Electrodes with the soaked electrolyte membrane and finally, you have the spacer that means, it is an insulating surface which will separate out the top casing from the bottom casing. So, that there is no electronic short circuit between the top surface and the bottom surface. and then you compress it in the form of a coin cell. So, even if you look at a typical simple coin cell which cost you 35, 40 rupees in the market, it is not a simple design. If you look inside, there are lot of efforts which have gone in.

Why? Because you have to synthesize the anode materials. you have to properly characterize those anode materials which before it can be used in such cells. Then you have to understand the use of electrolytes and which types of electrolytes will have to be utilized. And then there are various types of cathode materials that will define the voltage you can obtain from these coin cells. So, you will have different types of materials.

After all these things are understood they have to be brought together. Once they are brought together you have to understand how they will perform as a group. Will they have efficient reduction and oxidation reactions that would allow the motion of ions from cathode to anode or vice versa? Will the electrolyte be sufficient to facilitate the ion

motion. All these studies have to be undertaken before a simple coin cell can also go to a market. Then comes more complicated designs such as pouch cell.

A pouch cell you have the electrode material preparation that means cathode and anode, then you have an electrolyte, then you have the current collectors because these anode and cathode are mostly based on metal oxides which are insulators or to an extent semiconductor, but you must have an efficient electron extraction and insertion to have high performance. So, you have to have the current collectors typical ones are based on aluminum or copper foils. then you coat these electrodes. Once you have done that you have to roll these electrodes to obtain the desired thickness. Once you have obtained these electrodes you have to then separate these electrodes with a membrane which is soaked in electrolyte.

And finally, you have to seal these pouch cells so that they can be used, but when you have these spout cells which are being sealed then during operation you have release of gases. Then you must have efficient ways by which you can allow that the gases which are produced during the operation of these spouch cells can be taken out of these spouch cells otherwise that would lead to the expansion of the cells and you will see inflammations and after certain cycles you will have the bursting of the pouch cells which can be extremely dangerous. So, lot of studies have to be performed before pouch cells can go into market. Similar is the cylindrical cells. Typical cylindrical cell configuration is 18650 cells means 18 mm diameter and 65 mm of height with a nominal voltage of 3.

7 volt if you have these kind of lithium based cylindrical cells. Finally, you have the prismatic cells. These cells are very similar to pouch cells, but they are much thinner, lighter than cylindrical cells and pouch cells. till now they are mostly found in the shape of rectangular shape. The problem with these prismatic cells are that they are still not standardized and their safety remains a major concern along with the cost.

As you saw that these are the parameters which will define the performance of a battery. Same thing gravimetric energy density, volumetric energy density and specific capacities. We had seen in the previous lecture that these parameters can be used to compare the performance amongst different types of batteries let us say from lead oxide based lead acid battery or nickel metal hydride based batteries or nickel cadmium based batteries with lithium metal batteries or lithium ion batteries. So, the parameters remains the same and the definitions are also the same. You will have to calculate the OCV and also the nominal cell voltages.

If you look into the cell chemistry what is happening at the anode? Lithium is combining

with carbon and is giving you  $\text{Li}_x\text{C}$ . At cathode you have the release of lithium ions and electrons. During discharging you have again carbon becoming stable and lithium is being released electron flows from the external circuit those electrons reach the cathode and takes the charge neutral condition state of the lithium cobalt oxide to 0. So, you have a charge neutrality condition again stabilized. The theoretical capacity of the material needs to be estimated which is given by  $xF/nM$ , where  $x$  is the number of electrons transferred,  $n$  is the number of moles of a chosen electroactive component,  $M$  is the molecular weight of the same electroactive component.

So, if you have this formula you will find that typically for graphitic material based anodes you have the specific capacity of the order of 372 milliampere / gram and for lithium cobalt oxide, if you have 0.5 as the practical number of electrons transferred then you will find that these specific capacities are 137 milliampere / gram. It is therefore, very critical that you choose the right materials to design and fabricate the lithium batteries. There are various types of materials the lithium manganese oxide base materials, lithium nickel base materials, each of them have their own advantages and disadvantages, but you can clearly see that their crystal structures are very different. And if you have very different crystal structures that means, if the lithium has to move out from these structures their mechanisms would be very different.

As a result the performance of these electrode materials would be different. What is the result? You have different types of batteries in the market each having different types of electrons and therefore, their parameters are different. If you now see what is the importance of crystallography that which studied in first three weeks. If you do not understand the crystallography of these electrode materials, you cannot predict whether the material would be useful for battery technology or not. Because, you must have materials which are simulating channel like structures so that they allow the flow of the ion out of them and also receive it back.

So, you must understand the crystallography quite clearly. It is not that you have only one material by doping the material you can get new types of materials. and you will have new batteries which can be fabricated. You can have lithium cobalt base batteries, you can have lithium manganese base batteries, you can have lithium phosphate base batteries or you can have lithium manganese nickel cobalt base batteries and you will see the performance of these batteries can change. Depending upon the end user, you can choose the battery technology which is going to be useful.

Suppose, you want to have very high life that means, large cycling stability. and also high voltages obviously, you can choose between the phosphate or manganese based lithium

batteries. If you want to have lower voltages and stable self discharge that means, much lower self discharge then you can choose lead acid batteries. So, depending upon the requirement of the end users, you can decide the battery which would be useful. There are certain topics which are beyond the scope of this course, but one should really understand.

These are considered to be green technology, but are they really green? just to fabricate a material you have large number of steps. You are going to use various raw materials, you will use electricity from the grid which is still being produced from fossil fuel based generation units. So, your carbon footprint itself may become very high because you are dependent on the fossil fuel based electricity grid. Hence, there is a trend that to prove that these batteries are really green, the charging of these battery technologies or battery systems are actually being done using renewable based generation units also. So, they are being coupled with the wind or solar-based generation units and the charging stations are also based on renewable based charging or generation units.

Once the batteries have lived their life, how will you dispose them? Why? Because they are utilizing various types of toxic elements and after their cycle is over, you have completed the whole life, then you are going to have modified structures which can be toxic and difficult to dispose. So, what are the strategies you will use to dispose the batteries? That also needs to be understood. If you want to increase the lifetime of these batteries, then what is the strategy to regenerate these batteries? concept which is being used nowadays is the recycling of batteries. That means, you collect back the batteries, rip apart the batteries, extract the expensive components and then make the electrode materials again using those elements that have been extracted and then see if you can have the similar battery performance from the electrodes which were recycled out of the used batteries. Then lithium has its own disadvantages, limited resources, unequal resource distributions, cost.

Storage, stability. Hence, there is a strong need to move to technologies which are called as advanced chemistry cells that means, they are the cells which are going to have different ions which will take part in the storage mechanism. Some of them which are becoming extremely important for India are based on sodium ion or aluminum ion. and large number of studies are going on to stabilize such battery chemistries. Again it opens altogether new area of applications. Why? Because the energy densities of these batteries are quite different and they can add to the application range.

It also becomes important for us because it gives us the capacity to make new materials and then develop newer batteries. In this lecture, you must have clearly understood that there are various components of batteries which can be combined in different forms to have

different designs of batteries. and different configurations of batteries will give you different performance parameters. of the batteries will have similar working principles. It is only their parameters will change because the materials which you are using to fabricate these batteries would be different and as their electrochemical performances are different, the battery performance can be different.

The choice of battery depends on the end user and the materials will have to be suitably chosen so that you get the desired characteristics of a battery which can be supplied to the end user. These are the other references from where we took lot of literature and you can refer to them for more understanding. Thank you very much for listening to the first lecture of week 11.