

**Physics of Functional Materials and Devices**  
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**Lecture 42, Week 10**

**Battery I**

Welcome again to this fourth lecture of week 10. In the previous two lectures, we had discussed about the concept of supercapacitors and you had seen that it is a new concept seemingly, but it is quite related to conventional capacitors. The only difference is that the storage mechanisms in supercapacitors are quite different than what you consider while explaining the storage mechanisms in conventional capacitors that is the parallel plate capacitors. In supercapacitor, you had seen that it was basically the separation of the ions and then the formation of a solvated ion layer near the electrode surface which was giving you the formation of a parallel layers which was being called as electric double layer. and then you had another concept where you could exchange charges during reduction or oxidation processes. That could result in the appearance of the quantity that is  $dq/dv$ .

$dq/dv$  has the dimensions of capacitance and therefore, even though systems which were being fabricated using metal oxides or electrochemically active materials where redox reactions or faradaic reactions were leading to the formation of the charge storage mechanism that is variation of  $dq/dv$  was being called as pseudo capacitors. carbon based materials were becoming useful for electric double layer capacitors whereas, metal oxides, conducting polymers or composites were becoming useful for pseudo capacitors. And then we had discussed about the formation of hybrid capacitors where you had one of the electrodes having typical materials which had the performance of EDLC type formation mechanism and the other electrode having the pseudo capacitive behavior and that was leading to the formation of hybrid devices. The hybrid devices are believed to have higher energy density and power density compared to EDLCs or pseudo capacitors.

But if you look around and see most of the literature or books you will find that super capacitors are considered to be high power devices. That means, they are able to deliver high energy for short period of time, but if you are looking into applications such as your smart watches, laptops, mobiles or e-vehicles where batteries are being used will they be high power devices or high energy devices? Obviously, they would be high energy density devices. Why? Because you need continuous supply of energy with nearly the same output, but for a longer duration of time. So, if you have a laptop and if you have a battery backup of 6 hours, you want that the battery should have for at least 6 hours, it should have the energy output which is up to 80 percent of the maximum. and then slowly you will find

that the energy which is being delivered from the battery comes down and after some time the once the battery discharges you will have to recharge the battery of the laptop.

Same thing is true for your smart watches, your mobile phones. Hence, you have two types of devices. high energy devices and the high power density devices. Supercapacitors are what? Once again they are high power devices. Hybrid supercapacitors are moving towards a system which will have more energy densities while maintaining high power densities.

So, let us move on to the next topic that is batteries. Batteries are one of the most talked about energy storage technology in today's world. Most of you are familiar with the lithium ion based technologies, but is it the only battery technology which is there? and did it come in few years or it was a result of development from the first battery to the lithium ion battery, the development took more than 100 years or so. This one should understand. Why? Because it is imperative that you realize that for a technology to mature it is sustained research and understanding of the topic which is required before a technology can come to the market.

So, let us now move our focus on battery technology and we will start in today's lecture the concept of batteries. what are the batteries, what types of batteries are there, how do we classify batteries and then we will see that you we have moved on from voltaic pile type battery which was the initial battery to primary metallic lithium or lithium ion batteries. In today's world you will see that it is the secondary batteries which are becoming extremely important, but what are secondary batteries? This concept will also be introduced to you in today's lecture. What is this course? This course is based on functional materials and their use in devices. So, we must then focus on the use of materials in these batteries and what types of materials are used in such batteries so that we get the reliable and desired outcomes.

If you talk about desired outcomes then there must be some parameters which define this performance. And we will also talk about the basic parameters which are used to compare the battery performance and also define the battery characteristics. If you look into batteries, batteries are classified under two broad headings. One is primary and those batteries which are used once and then disposed are classified under the heading of primary batteries. Then comes secondary batteries or rechargeable batteries.

These are the batteries that can be used and then recharged not only recharged once, but they can be recharged multiple times and they can have significantly large number of cycle life. For example, if you look around the typical cycle life for the lithium batteries which are being mentioned is 1000 or more. For the number 1000 it does not seem to be very large, but if you convert in terms of years you are talking about a period of nearly 3 years or slightly less than that. So, you are talking about 1000 cycles if you charge each battery

once a day and then if the battery characteristics remains nearly the same for 1000 cycles. One cycle means charging and discharging together.

So, if you have to charge a battery only once a day and then you can operate this battery for 1000 cycles that means, you will be able to run the given battery for 1000 times and that means, you will be able to use effectively this battery for nearly 3 years and that is where the advantages of rechargeable batteries have come into picture and there are various types of batteries which are available in the market now. So, as I mentioned if you move from for example, lithium battery, lithium metal or lithium ion to nickel metal hydrides to nickel cadmium to lead acid or sodium ion, zinc ion, zinc air, lithium sulphur these are various types of batteries. We will see some of them in detail in some time, but I just mention these names. Then how do you compare the performance of these batteries or one battery from the other? There are parameters which are used to define the battery performance. The first one is the gravimetric energy density in terms of Wh/kg This is the energy density which is defining the amount of energy that can be stored per unit mass of the electrode material.

That can be stored why because battery is a storage technology. Then comes the volumetric energy density as the name suggest it is mentioned in watt hour per centimeter cube. This would be the energy density that would define the amount of energy that can be stored cubic meter of the battery volume and then you have the specific capacity in milliampere hour per gram. This defines the amount of electric charge in milliampere hour that the material can deliver per gram of the material. Why am I stressing on the terms material? The reason being you will find that the performance of the batteries are being defined with respect to the performance or response characteristic of the materials which are used to fabricate either the electrode or the electrodes and that is where the advantage of materials come into picture.

The moment I say material what do I indicate? It clearly tells you that if you change materials and if you choose suitable materials which can be used to store materials. certain ions or release certain types of ions, they can either act as the anode that is the electrode which will store the ion which will be released from the cathode. So, you can tune that and you can move from one type of battery to the other. Now, you choose different types of cathodes itself with different capacities to release the ions, then obviously, you will get different battery characteristics. You choose different kinds of host.

which will store this ion which is moving towards it. What will you get? You will get different types of storage capacities and therefore, what you will have by tuning the performance of the battery you can easily have the new types of batteries and that is where the whole idea is coming in. So, you can have lithium based batteries, even in lithium batteries it is not only lithium cobalt oxides which are used. You can use lithium nickel oxide, you can use lithium manganese oxide or you can use manganese nickel oxides or

you can use nickel manganese cobalt modified lithium hosts to deliver lithium ion and these are called as lithium NMC electrodes. So, based on these materials you will have different types of batteries.

So, can you now think why you always get new types of batteries in market these days? One company will come and say that now we have a new battery. Why? Because if you can make new materials which are going to perform as per the requirement of the battery technology, what will you get? You will get a new battery. then you have the battery. So, obviously, battery would be something which would be giving you the voltage. So, nominal cell voltage is the voltage of the fully charged cell or combination of cells which gives you batteries.

When it is delivering the rated capacity at a specific discharge rate. So, you must also define the discharge rate. What is that? The rate at which you are asking the battery to release energy. So, suppose you want to accelerate a e-vehicle at a very fast rate, then you will be asking extracting larger amount of energy from the battery in the same amount of time where you are accelerating the e-vehicle at a much lower speed. Suppose, you take the vehicle from 0 to 100 km/h in 10 seconds and then you take the vehicle from 0 to 100 km/h in 10 minutes.

Obviously, the rate at which you will extract energy from the battery would be very different and hence you will have the rated capacities at a specific discharge rate which could be different. Then you have the open circuit voltage. This is the difference of electrical potential between two terminals of the battery when it is disconnected from all the circuits. So, you just take a battery, take a voltmeter and measure the voltage which you are getting when no load is applied across the terminals of the battery. If you look into the primary batteries.

One of these batteries which was very popular and you have read it from school days is the Leclanche cell or the manganese cell that was discovered when in 1865 nearly 160 years back by Leclanche who was a famous French engineer. What was the construction? You had zinc based anode, an  $\text{MnO}_2$  based cathode and an aqueous electrolyte which was based on ammonium chloride and zinc chloride. And when you connected the terminals, you could observe an EMF which was of the order of 1.5 volt. Now, when you had this cell obviously, you wanted to have much higher voltages.

Then you could tune the performance by changing the acidic electrolytes by alkaline electrolytes and you had the discovery of alkaline batteries. this give you the advantage of improved capacity. In addition to that you also observe improved discharge profile at the same voltages. So, you could have a much improved discharge profiles. Then if you see one of the most common secondary batteries which you see in the market is the It was proposed by Plante in 1859, again nearly 160 years.

Typical construction, you had the lead peroxide-based anode, a lead-based cathode and a weak sulfuric acid as an electrolyte. And typical EMF which you can obtain from these cells, one of the cells is 2 volts and if you add and these cells and then you have a series of cells giving you batteries, you can have various types of lead acid batteries. Then around 1980s came the technology that is nickel cadmium which was giving you 1.2 volts and you had your AAA or AA cylindrical cell type batteries which were coming into market with a specific capacities of 1200 milliampere R ratings. The problem with nickel-cadmium was that it was harmful to environment because of cadmium and so, it was then replaced and you had in 1990s you had the nickel metal hydrides with similar voltages which came into picture.

Same cells you see these are cylindrical type cells. And, then came a major breakthrough where you could have 3 volt lithium based secondary batteries with much higher energy densities, compact design and light weight which revolutionized the way we talk about the battery technology today and the impact is visible all around us. Therefore, if you look around this battery technology we will find that there has been two major milestones. One, the development of secondary batteries and then the advancement of working voltage to 3 volts. Why 3 volts? Because the energy density would be energy is given as  $(1/2)CV^2$  So, if you are having for similar C values if you are having a nominal voltage of let us say 1, then you would get  $E \sim C/2$  joules.

But if you had 3 volts, then you would have  $9 C/2$  joules. So, you could have very high energies which were being obtained from these batteries. But is it a new technology? It is always important to realize that what you are actually reading has been an effort of many people and the history of the whole technology development can give you an idea about the future direction which this technology will take. So, if you see the first report or possibility of having a current flowing between two electrodes, it was probably coming in from the Galvani's experiment on animal electricity. What they found that if you have the muscles of the dead frog legs, when you have an electric spark then it twitched.

These they believe was the energy that drove this contraction came from the leg itself. He named this as animal electricity that is when two different metal were connected in series with a frogs leg to one another they were seeing the twitching of the leg. So, two different metals like brass and iron were actually stuck into several limbs of the frog and when a wire outside during an electrical storm, it indicated that the limbs of the frogs would twitch and it was believed that the electricity was coming from the legs itself. Then came in around 1800s by Volta who was friend of Galvani, he disagreed, he said no this is coming in because this is a phenomena which was being caused by two different metals which are joined together by a moist intermediary. So that means, moist intermediary what you call nowadays as aqueous electrolyte.

For this Volta took two-disc zinc and copper and place the disc on a cloth or even a paste board or a filter paper, moist the filter paper or the cloth with brine solution or vinegar what was seen that you could obtain voltage. So, if you had copper as cathode and zinc as the anode you could get the voltages. So, obviously, it was not the animal electricity it was because there was a moist intermediary which was connecting the two metal which were separate. What was happening? The Volta's original pile had certain disadvantages. One of them was you could clearly see that they would lead to leaking of the electrolyte and causing short circuits.

Why? Because once you had the heavier plate pressed on the cloth, then the disc compressing the So, cloth would push the liquid outside and there would be a short circuit between the two electrodes. Then you had the hydrogen bubble formation at the copper which steadily increased the internal resistance and then the overall performance degraded. As long as the electrolyte was present there was continuous chemical reactions. and when there was continuous reaction the metal was degrading. What was the consequence? You would see that the battery eventually was losing all its performance and had a short cycle life.

This is a typical Voltaic pile which is displayed in Volta's home in Italy and was initially used to describe the concept of electricity flow or the flow appearance of voltage between two electrode plates which were dissimilar. Then in 1836 came the Daniell copper zinc base cells And here you had these copper and zinc electrodes which were dipped in the solution of copper sulfate and sulfate respectively. And so, what was happening at the cathode you had the discharging of the copper. and you would get the copper solid plus voltage of + 0.

34 volts. At the anode you had the zinc solid giving you the zinc ions plus 2 electrons. So, you had the - 0.76 volt. The salt bridge provided the ions to move from one end to the other during charging or discharging. The basic advantage of this cell came that there was no hydrogen bubble that was observed and so, you could eliminate the problem of hydrogen or oxygen evolution.

Immediately this became more reliable than voltaic pile and had a longer life cycle. Then in 1859 you had Plantet discovering the famous lead acid batteries and it is still and it will continue to control the battery market for many more decades to come because if you look around there is a massive movement which has been. started by many companies worldwide and even in India where they are talking about regeneration of batteries. Not the lithium ion batteries, the lead acid batteries which are already integrated into the storage networks. if they are dying or losing their performance after 5 years rather than disposing them is there a protocol which can be devised to regenerate their performance and reuse them if not for another 5 years for at least 3 years or so.

That means, you will have a battery which will have a lifetime of around 8 years or that if that protocol becomes successful it would be a major impact player in the whole energy storage market. And these are the typical anodic and cathodic reactions which take place which you have been seeing for many years since your school days. But the major disadvantages which are still there that it is the weight and the size of the batteries which continue to be a limiting factor. In addition, you have the cycle lives which are still quite low and the gravimetric energy densities are also low in compared to other technologies. After the discovery of lead acid battery came the nickel-cadmium and you had the Swedish scientist, the scientist name was Waldemar Junger, who invented the battery in 1899.

So you had the nickel oxide or nickel hydroxide based cathode and cadmium based anode. And you had the reactions at the positive plate and the negative plate resulting to the appearance of voltage which were of the order of 1.2 volts to 2.7 volts. And the advantages were in comparison to lead acid batteries that you had slightly higher gravimetric energy densities.

The volumetric energy densities were much higher, the voltages were slightly lower, but the cycle life was significantly higher if you compared the batteries till, they had 80 percent of the initial capacity that is if you define the initial capacity in the first cycle then till which cycle the batteries were able to have 80% of the initial cycle value. In addition, the nickel cadmium had much slower self discharge, but they had a fast charging time advantage. So, they could be charged at a much faster rate while they depicted the capacity to retain the charge for a much longer period, but as we said that because of the use of cadmium this became quite controversial and you had to discard this technology for large scale usage. Then came the nickel metal hydrides in 1989 and these are still very important in today's e-vehicle market. You will find that many companies which are launching their vehicles in India.

They are talking about strong hybrids. That means, they are not fully on batteries, but they have a significant contribution which will come from the battery technology along with the fossil fuel engine. these are strong hybrids. Many of these vehicles are actually based on nickel metal hydride batteries and not lithium ion batteries. So, they continue to have tremendous applications and now those applications are going to become even more important as the market for such batteries has just begun to grow. Similar concepts you had the anode, you had the cathode and you had the alkaline electrolyte and the corresponding reactions at the anode and cathode resulting in the appearance of voltage between the anode and cathode.

If you compare nickel cadmium with nickel metal hydrides, you will see nickel metal hydrides much higher gravimetric energy densities, much higher volume energy densities, then you had similar battery voltages, but cycle life of nickel metal hydrides are slightly lower than nickel cadmium, but they are not like that they are very very small. So, they still

have significantly much larger cycle life than your lead acid batteries. So, if you have lead acid batteries which have a cycle life of 500, these nickel metal hydrides have a cycle life of at least 1000 or more that is two times that of lead acid batteries. The self-discharge is slightly higher than nickel cadmium, but they have similar charging times. The massive advantage is that their toxicity is much less than that of nickel cadmium and as a result of this you will find that.

Nickel metal hydrides have become extremely important and are going to be used in many applications in time to come. So, if you compare the three technologies the lead acid, the nickel cadmium and nickel metal hydrides, you can clearly see that the charging times are quite low in nickel metal hydrides. The cycle life are higher in nickel base batteries, the volumetric energy densities are much higher in nickel base batteries in addition to the gravimetric energy density. In addition, you will find that these batteries are used in a wide temperature range. So, if you look around you have during winters if you take Kashmir region in winter you will go around -10, -15.

During summers it can go nowadays up to +40 or +40 (+-) few degrees. That means, if you have an e-vehicle which has to operate in this region, then you should be able to operate it. That means, it should operate in -10 to 20 degrees degree conditions to +40 to +50 degrees temperature. Why? Because +40 degrees is the ambient temperature, but when you have all the motor running, the axle running, you had the engines which are there, you have the air conditioning unit which is running, then the temperature inside the compartment where the battery is being hosted may actually be slightly higher than the ambient temperature. And this is what you have seen that when a car comes in and it has just reached its destination after running let us say 10 kilometer or 20 kilometer journey, then if you put your hand on top of the hood of the car, you will get burnt or you will feel that the top of the hood is extremely hot and the temperature is much higher than the ambient condition because there is a heat generation taking place by the running of the motors.

So, even if the ambient temperature is around 40°, you must ensure that the batteries which will see around +50 to +55 or up to 60°temperature, they should be able to operate in this condition and all these batteries are able to operate in those conditions. The major disadvantage of these batteries is that they are aqueous based batteries. that is aqueous electrolyte. If you have aqueous electrolyte that which is based on water, then you have the dissociation of water which is occurring at around 1.2 volts. So, if you go beyond that voltage, then the water dissociates and electrolyte is no more useful. you will have a limiting factor in the operating voltage which you can get. By playing with the work function of the electrodes you can slightly increase the voltage which you can obtain from these batteries, but use of a aqueous electrolytes are major disadvantages in these batteries and the problem of the use of aqueous electrolytes was addressed by the noble with prize winning Japanese chemist Professor Akira Yoshino who started the work on non aqueous electrolytes. So, now you can have non aqueous electrolytes and because of that

you can have much higher EMF values which can be obtained. And with these batteries people have now obtained lithium metal batteries which are primary batteries not secondary batteries, but they have much higher voltages.

Even if you use these lithium-based batteries about which we will talk more in detail in the next lecture, there are certain limitations. Those limitations include thermal runaway or short circuiting between the electrodes due to the formation of dendritic structures and that leads to the short circuiting and the problem of explosions in such batteries, but then there are strategies which can be used to address these issues. We will talk about this in the next lecture. So, in the next lecture we will talk about lithium ion batteries and you will see why materials are so important to make this technology a successful technology. For the work in the field of lithium-ion batteries, three famous scientists Professor Whittingham, late Professor Goodenough and Professor Yoshino were awarded the Nobel Prize in Chemistry in 2019.

So, in one slide if we have to put the development, you will find that from 1800 to 1990 when Sony first released the first commercial secondary lithium-ion batteries, there was continuous work. So, it was a work of nearly 200 years before we reach the lithium ion technology. And lot more needs to be done before we can go and have the battery based storage landscape or wide scale usage of e-vehicles which are using secondary batteries. These batteries you already know have large number of applications which we will talk about in the next lecture. I have just put this slide so that you know that it is important to understand the operation of these batteries, how they are constructed, which materials are used and then only you will be able to use these batteries for various applications and the market is continuously growing and hopefully the growth will continue for many more decades.

So, that we can mitigate the issues of climate change by using more cleaner and more efficient storage technologies. Hopefully you have understood the difference between primary and secondary batteries. There are various types of batteries. It has been a long timeline over which the research had to be performed. This led to discoveries of various types of batteries and the ones which we use today are mostly based on lithium, but future is for advanced chemistry cells beyond lithium and India is moving towards cells which would be based on sodium or aluminum.

These are the differences based on which we prepared the lecture notes today and you can read them more to develop better understanding. So, thank you once again for attending lecture number 4 of week 10.