Non-conventional Energy Resources
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Lecture – 31
Lithium ion Batteries

Hello. In this class we will look at the Lithium ion Batteries. You may very well be aware that lithium ion batteries are presently extremely popular in terms of mass market usage, and for a several you know applications they seem to be the appropriate type of battery to use. So, for example, almost all our mobile phones are presently coming with lithium ion batteries, and if you look at the present generation you know electric vehicles electric cars, that people are trying to you know put into the market in large scale. The battery of choice as of now seems to be the lithium ion battery.

So, there's considerable focus on this battery chemistry and a lot of research goes on in it, lot of R&D work goes on it and it is being used extensively by the public. So, it is in this context that we will focus on this particular battery chemistry. Although, we will you know we do look at the all the chemistries in general, but this is battery chemistry that is very you know current in terms of the level of interest that people have in it. In fact, the extent of interest on in this technology is so high, that specific I mean countries are countries as well as companies are actively searching for you know sources of lithium and trying to block it so, that it is now accessible only to them, to block in the sense buy exclusive rights to it.

So, many companies are trying to do this even countries are trying to do this then you suggest that enough example China apparently has been spending a lot of effort trying to buy you know sources of lithium. So, to speak; so, as essentially they invest there. So, that they get exclusively right to it. So, that kind of a thing which is typical business you know processes those kinds of things are on.

So, that's the extent to which this is technology of interest and you know affects everybody from a common man to you know corporations that are participating in it and nations which feel that you know the future lyes with the electrical energy storage associated with the electrical energy and that the lithium ion battery is going to be critical aspect of this energy storage process ok. So, it is in this broader context that we will look at the lithium ion battery technology.

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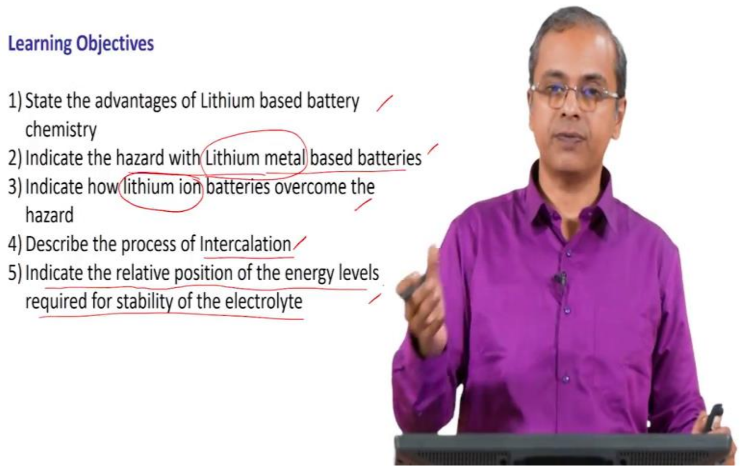

So, our learning objectives for this class are that we would like to state the advantages of the lithium battery based chemistry, lithium based battery chemistry. So, to get an idea what is the advantage, why are you people you know so excited about it, and you know spending so much time on it. And we would also at the same time like to indicate, what is the hazard? There is some hazard associated with lithium metal based batteries. So, we would like to get sense of that what is that hazard, there is one standard the issue with lithium battery. So, that's something that you like to look at. And I would like to say that you know even though if you are not careful they all look the same; there is actually a difference between what you would call as a lithium metal based battery and lithium ion battery.

So, these are not the same I mean. So, that is the point that I would like to highlight here and we will see as we proceed, why this is a difference ultimately it's the same element lithium that is being used its just the form in which its being used that is different and therefore, that changes issues associated with it, that changes the manner in which we work with it etcetera. So, things like that. And we would there is a particular process known as intercalation. So, this is something that I will describe to you, because it's very fundamental to how these lithium ion batteries work and may continue to play a role in you know future versions of the lithium ion technology.

Therefore, we will like to look at it. And as a general discussion I would also like to indicate this concept of the relative position of energy levels required for the stability of the electrolyte, we will discuss it in the context of lithium ion batteries, but its exactly the same for any battery system. And therefore, that's something that we should be aware of. So, these are our learning objectives, the advantages of the lithium battery chemistry, the hazard associated with the lithium metal based batteries how the lithium ion batteries are overcoming that hazard that what is this process of intercalation, and the relative position of energy levels associated with these different parts of the lithium ion battery.

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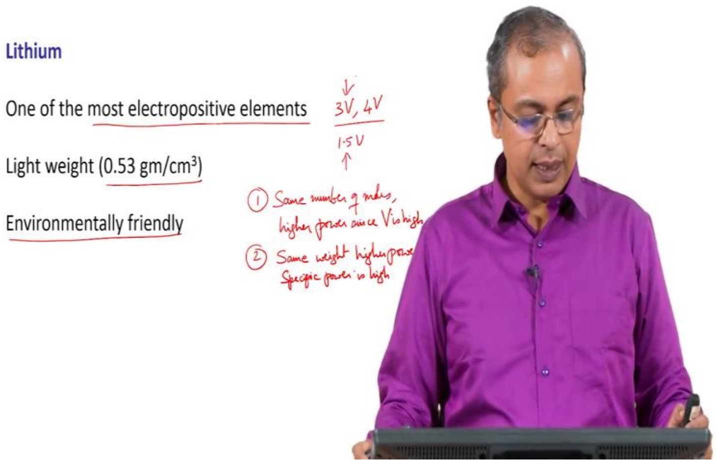

So, that those are a learning objectives. So, why are people excited about lithium, why is the lithium ion battery such an interesting technology to spend so much of time and effort and you know public interest is being built in it and it built on it. So, why is this the case; one of the most electropositive elements that you will find; so therefore, it is very eager to hand off an electron.

And therefore, if you look at the standard electrochemical series, it is you know very anodic its extremely anodic and so you, you can couple it with almost any cathode that you would like to use in this case and you will get very high voltages ok, so extremely high voltages. So therefore, when you compare against any other battery, with lithium ion based batteries you are looking at voltages of three volts, 4 volts etcetera something like this. So, this kind of a voltage you are looking at as the voltage you will get from the battery.

So therefore, if you draw the same amount of current right and compare it versus some other battery chemistry which is only giving you about 1.5 volts. So, for the same current you are actually getting double the power right. So, double the power you will get. So, 3 volts if you are using a 3 volt battery versus a 1.5 volt battery. For the same amount of current that you draw out of it you are getting double the power and therefore, power density is high. So, the you know specific power is high power for per unit mole that you will get much higher with a lithium based system than with any of the other computing systems that you might consider.

The second thing is that it is very lightweight. The element is very lightweight its only 0.53 grams per centimeter cube is the density so in fact, it is only as dense as wood some versions of wood are only this are about as dense as this. So, it is extremely light and therefore, when if you cover if you couple the high power that you will get with the low weight associated with it, you are getting high specific power ok. So, power per unit weight on a specific on a specific mass basis the power the specific power that you will get per unit mass is high ok. So, the power per unit mass which is the specific power on a mass basis is very high in this case right. So, power by weight.

Therefore, that is very exciting again. So, this means with a very lightweight battery you will get a lot of power. So, first of all for the same number of moles of the element, you get more power. So, same know same. So, when I am comparing against some other battery technology. So, you will have same number of moles, higher power since voltage is high okay that’s the first advantage we have. Second thing is because it is light same weight higher power.

So, specific power is high ok. So, specific power is high. So, these are two very interesting concepts. So, for the same weight you get higher power and same numb same number of (Refer Time: 08:20) moles you get higher voltage. And for the same weight you actually have even more moles, because the element is also just you know very low in the periodic table; so hydrogen, helium, lithium.

So, it is like the third element in your in your periodic table. So, it is going to be for the same weight same number of grams you are going to have more moles. So, same number of grams as some other anode material you will have more moles of lithium. The more moles of lithium will also give you power at much higher voltage and so, you get much higher power right.

So, higher specific power in more than one way you get. So, that’s the big advantage and also it is environmentally friendly, it unlike many other chemistries that are commonly looked at, which are also chemistries that are there significantly in the mass market. So, for example, for all our car batteries most of the time we are using lead acid batteries even as of today that is the battery that starts the car it’s not yet an electric car, but just to start the car there is always a battery even though we may have a petrol powered vehicle in our car there is a battery. That battery is mainly went meant to start the engine, when you first time start the engine as you start the engine to start I mean before you start driving that battery is typically lead acid.

The batteries which are mostly sitting in our homes as part of Uninterrupted Power Supply system’s UPS systems are also lead acid batteries. So, there is a significant usage of lead acid batteries around the world. So, it’s a popular chemistry popular from the prospective that is a very prevalent chemistry, lot of places they use it mainly because you can draw lot of current from it. So, that chemistry is around, but it is hazardous because you have acid which is hazardous and you have lead which is hazardous. So, of course, they do a lot of recycling of the lead, but still the entire industry is hazardous for that purpose for that purpose for that reason.

Whereas, lithium that is not the case. So, it’s not at all hazardous and it is relatively safe the other popular battery system is the nickel cadmium battery, there again you have cadmium and that is also toxic. So, in comparison to lead acid battery and nickel cadmium battery, lithium based batteries are when we very environmentally friend. So, when you look at all this the high power the that you get the high power density that you get the fact that you know its environmentally friendly all these things you take into account that is what causes this battery technology to be extremely popular right. So, that is the point about it, its right.

So, now we would also like to understand what are some issues associated with it. So, we will look at that briefly.

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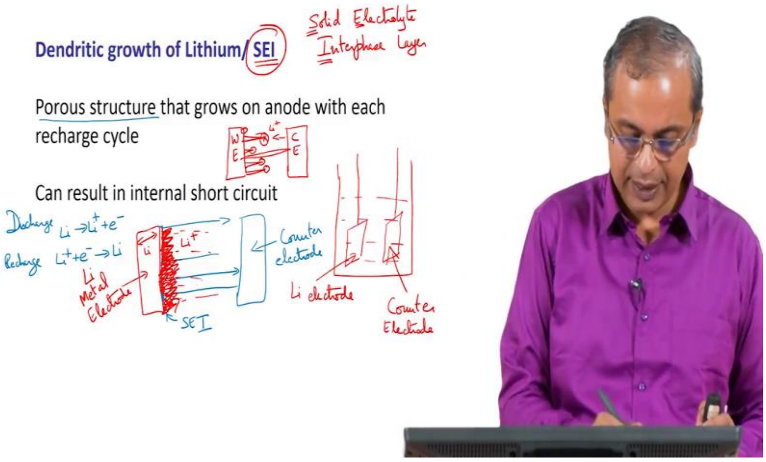

So, the point is when you when you have a highly reactive material like lithium or even for that matter aluminium let's say. So, if you take that the moment they are exposed to atmosphere they will immediately react to the atmosphere. So in fact, lithium you cannot exposed to moisture and air it is just rapidly react. So in fact, people who work with lithium ion battery materials do not work in the open lab they will not work on a tabletop like this, you will not you will not just have a experiment with sitting in open air right.

So in fact, if you go to any lab that is working on lithium ion batteries, they will have a glove box. So, glove box would be one you know it is like a big chamber which is which has transparent glass on all sides usually some you know perspex kind of glass, and it will have to be gloves through which you can we can put your hand into the glove and you can reach inside the chamber. So, both hands you can put inside the chamber, but you will be standing in front of you there is a plexiglass. There is a glass or a perspex glass through which you can look inside. You can look inside and see what this inside it will be clear, but your hands will be reach and only using a glove.

So, there will be a big glove with both hands which will be tied to this plexiglass. So, it is sealed the container is fully sealed and only because of this flexible gloves we are able to reach inside into some experiment. So, inside the container you will have inert atmosphere you will have argon typically and it will be dry atmosphere. So, they will actually have chambers below that you know glove box which is continuously drying that air, whatever not air the atmosphere that is inside the glove box and keeping it completely humidity free. You have to have it less than PPM of PPM level of humidity only then you can work on it, otherwise its extremely dangerous the material react very violently with humidity.

So, therefore, that is the way in which we have to work on it. So, when people work on this lithium ion technology and make cells which then they test we were talking about you know charge discharge curves etcetera in our last class, but when they do all that, the all of that has to has happened only in with the cell that is sealed that that is not exposed to the atmosphere. Even the batteries that we have in our mobile phones etcetera are suppose to stay sealed they are not suppose to be opened and exposed to be atmosphere. So, there all sealed. So, in the same case this is also sealed. So, normally what they would do is, at the cell would be constructed inside this glove box.

So, it will be kept in a way in which it is put together in the glove box with the electrodes etcetera sticking out, but I mean or contacts to the electrodes the current collector sticking out the electrodes will be completely immersed in the electrolyte and the whole thing will be sealed. And in a you know your best case scenario is such that your test equipment will be outside the glove box, just outside the glove box and wires will be connected to through the glove box into this experiment that is sitting inside the glove box.

So, electronics will sit outside the cell will sit inside and through that we will run the test or at least you should seal the cell completely and then you can take it out of the glove box. So, that it is now you know completely sealed there is no danger of atmosphere going in, and even then keep it some kind of in inert location where you have some gas flowing and then run the test. So, it is a activity that you have look carefully with respect to the environment that the lithium is exposed to mainly because lithium is extremely reactive.

So, what happens when we create a cell? So, you have a cell, let’s assume I am in inert atmosphere I have made this cell in an inert atmosphere and then we have the electrolyte here. So, let’s say we just put one electrode of lithium here another electrode of something some counter electrode here. So, I will just call this the lithium electrode and this is the counter electrode right. So, as soon as the lithium electrode sees the electrolyte, what happens is the surface of the electrode reacts with the electrolyte ok. So, it immediately reacts with the electrolyte, and forms a passivating layer reacts meaning it gets oxidized by the electrolyte and it forms a passivating layer.

This layer is called the SEI layer or Solid Electrolyte Interface layer. So, that is this Solid Electrolyte Interface layer that is this SEI. So, the SEI layer or the solid electrolyte interface layer is the layer that forms because the lithium metal reacts with the electrolyte. Now this is both a positive and negative it is positive in the sense that what happens is this layer that forms is a continuous adherent layer and therefore, protects lithium from further reaction with the electrolyte. So, it forms on the surface of the electrode, and then prevents further reaction with the rest of the electrolyte. So, for example, if this were the side view of the electrode and this is where the electrolyte is, the SEI will form at the surface.

So, it will form right here. So, structure like this will form. So, this is the SEI. SEI layer this is the electrode itself ok. So, the electrode lithium electrode in contact with the electrolyte forms a solid electrolyte interface layer. So, it is good because this layer then prevents the rest of protects the rest of the metal. So, this rest of the metal is protected, only the top layer of the metal which is in contact with the electrolyte passivates like this. So therefore, it is protected, but the bad thing is it now adds to the resistance for the path of the ion. So, the ion that is inside here. So, lithium that is sitting here which has to become lithium plus as it goes into the electrolyte, it has to pass through this layer and go through.

So, it usually adds to the impedance of the the cell; it adds to the impedance of the cell which is basically obstruction to the flow of current. Impedance is the most general term like you are used to resistance in a in the context of flow of electrons, that resistance is also obstruction to the flow of electrons. So, you can have any species that might carry charge in this case an ion is carrying charge. So, Li plus is carrying the charge. So, you say more general term we say impedance which is basically an obstruction to the flow of current. So, the impedance of the cell goes up and ideally we want low impedance because otherwise we are wasting energy going past is impedance every time there is impedance.

So, if you say there is an impedance of value r, we are having an IR drop associated with it which is wasted electricity. That is electricity that we could that is wasted potential voltage of the cell is partly wasted in getting past this barrier instead of doing work with the whatever else that you want to do you wasted here right. So, this is the thing, but. So, this is the positive is that it protects the electrode, negative is actually two parts it is the negative.

One is that your adding impedance to the cell and the second thing is you are actually irreversibly consuming a little bit of the electrolyte as well as a little bit of the electrode. So, this SEI layer then is essentially a little wasted layer, its a wasted surface layer because it is used up a little bit of the electrolyte and therefore, you know irreversibly changing in the electrolyte in some way it is also used up a little bit of the metal.

So, in that sense it is also not a very positive thing, but it protects the electrodes are there that is fine. But there is another problem here so, there is the SCI. So, that is what happens when you put this lithium as soon as you put it into an electrolyte because it is so, reactivate with forms this. But let’s say you continue now having done all this you make the cell. You make a cell and then you start cycling it. So, what happens is every time you send lithium ion in and out of the cell.

So, lithium ion goes this way and then it comes back this way. So, you have some counter electrode here. So, every time the ion goes from the main from the working electrode which is lithium to the counter electrode and then comes right back the why should it come back? When you when you are discharging it is going on way and your recharging it is coming back. So, this is what we are doing charging discharging, charging discharging that we do we keep on shuttling between the two electrodes we shuttle the ion between the two electrodes. Now every time it comes back, it is trying to come from Li plus to lithium.

So, during discharge so during discharge Li goes to Li plus plus e minus. E minus is going with the external circuit. So, that is what a process is. During recharge you are doing the opposite reaction Li plus plus e minus gives you Li ok. So, this is being done by pushing electrons in from an external power source, you push electrons into the lithium electrode it will take back the lithium ion and it will form lithium metal. So, now, for that to happen the lithium ion has to actually go through this solid electrolyte interface and go back to that metal. So now, when this happens when you keep doing this actually sometimes it doesn't go through properly or it goes in and forms a different kind of a structure, it doesn't it doesn't plate it in a flat manner that is the problem with the lithium metal.

When it comes back and it plates on the lithium this lithium ion comes backs and plates it on the lithium metal, it would be nice if it plated back as a flat structure unfortunately it a thus I mean huge amount of experiment experimental evidence that shows that when lithium ion comes back and plates back on the metal, it does not plate as a uniform flat structure instead it forms a porous structure. So, what it means is, you are actually having this lithium metal sort of form like this, some kind of a porous structure is happening. So, with the progressive cycling and on top of it again you form some solid electrolyte interface, because now we have much larger area, so this continuous. So, with every cycle this becomes a more and more porous structure that is growing ok.

So, it is continuously going with every cycle this continues to grow and there are various reasons for it. One of the reasons the reason one of the reasons that it is growing is because the front most point of the. So, we it is an un even surface right its an un even surface, the front most point of that surface that is front most with respect to the counter electrode. So, I have working electrode here, I have counter electrode here. The front most point of this electrode is the closet to the counter electrode right. So, I have working electrode here and I have counter electrode here. So, I will say this is the counter electrode this is working electrode W E is working electrode C E is counter electrode. Supposing this is not a uniform surface, but I have a sharp point like that.

Now, this point is closest to the counter electrode. So, when the ion comes back Li plus comes back, it is it is easier for it to plate this point ok. So, it will continue to plate at this point. So, any rough surface it has. Multiple surfaces it will more easily plate at these points then come all the way up to here and plate.

So therefore, the moment it becomes uneven the progressive cycle makes it more and more uneven, it encourages the unevenness it builds on the unevenness. It is already uneven, it does not go back the second cycle does not make it flat the second cycle makes it even more uneven because whatever is uneven is you know being built on and that is what is progressively being built on. So, it continues to grow. So, you may have a situation where eventually it does a short circuit ok.

So, that is basically what I am going to show you here, and that is what we are saying by saying that this kind of a growth can result in an internal short circuit.

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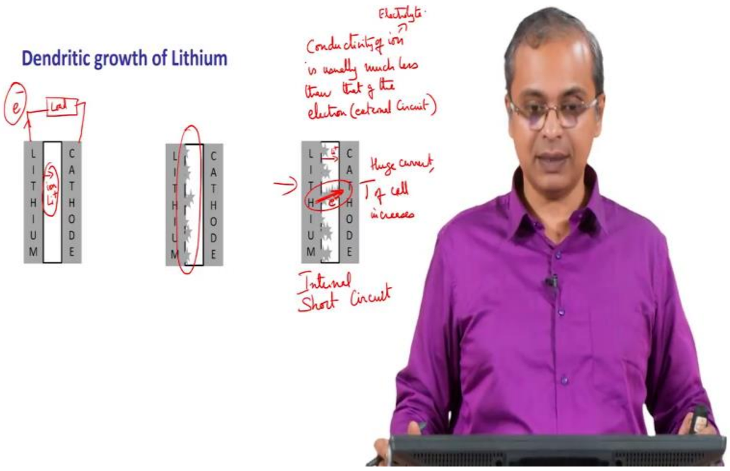

So, for example, if this is what this is just a schematic of what is happening, you have the lithium metal here you have the cathode here. So, let’s say you cycle it then what happens is, you start seeing this uneven structure here right. So, lot of. So, this is called dendritic growth, this kind of growth is called dendritic growth because it represents as structure that looks like dendrites and that is this kind of a structure this kind of a you know pointy point structure which is growing in different directions; so dendritic growth. So, you can see that this is not plated back as uniformly as you see here. This is a nice uniform surface interface a flat surface which is now become a you know pointed pointy surface which is highly uneven.

So, if you continue this you can see now you know for example, this is a little bit ahead this will keep growing faster with progressive cycling every cycle. So, initially it is okay first cycle, second cycle, third cycle as you continue you will eventually reach a situation where it looks like this. You have an internal short circuit you have an internal short circuit ok. So, what this has what is happened is that, with progressive cycling the lithium metal did not plate flat flatly and then eventually found its kept growing in definitely and makes in internal short circuit, this is a very dangerous situation. A very dangerous situation because now there even see normally you have to connect an external circuit, normally we connect and external circuit we put a load and the electron travels like this and the ion travels like this ok.

So, the moment you remove the load, the battery is an open circuit. If there is no load there that there is battery is an open circuit the reaction stops, because the electron also has to flow, the ion also has to flow, both those steps have to happen for charge neutrality to be maintained only then this circuit is complete the reactions are complete and the reactions will take place. If you open up the circuit outside there is no path for the electron to go everything stops right.

So, now, when you have an internal short circuit both of them can happen, you can have electrons just go across like that and you can have ions that go across like this. So, you no longer need an external circuit, everything is happening inside the cell. So, current will build up very fast it will flow very fast, you have huge amount of current going like this because nothing is this is just metal, you have just metal between you know positive and negative of an electron you are just put metal. So, this is a short circuit and it is inside the cell; so its internal short circuit.

So, this is actually a dangerous it leads to a battery explosion because what happens if the normally in in these batteries, the conductivity of the ion is usually much less is usually much less than that of the electron. The ion this is of course the electron is in the external circuit the ion is actually in the electrolyte ok.

So, ion is flowing through the electrolyte, electron is going through the external circuit which is what we have here. The conductivity of the ion is usually much less than the conductivity of the electron. So, that is another reason why the current is not so, huge ok. So, otherwise the current can be huge interestingly the conductivity of electro lights our ionic conductivity of most materials increases with temperature ok; unlike electronic conductivity, electronic conductivity actually decreases with temperature ionic conductivity increases with temperature.

So, now when you have an internal short circuit, you have a lot of current going through this internal short circuit will have a lot of current going through a pathway that pathway heats up. So, because of this huge current, temperature of cell goes up of cell increases.

If temperature of the cell increases it increases the conductivity of the ion. If we increase the conductivity of the ion the current in the cell further increases ok.

So, this is called a thermal runaway this is called thermal runaway ok. So, that that is because you are having internal short circuit, because of the internal short circuit lot of current is flowing in that path. Because lot of current is flowing in the path temperature of the cell is going up, temperature cell you can physically feel has started becoming warm because it has become warn the ionic conductivity has gone up which was the slowest step previously now that has gone up.

If that has gone up the current in the original short circuit goes up even further ok. So, and then again it heats up even further, further ionic conductivity goes up. So, this is a you know unending cycle, it just increases rapidly and it can explode the lithium battery can explode basically it has an uncontrolled reaction it can explode. So, you have you must also understand this happens after a few cycles it is not happening at the beginning.

So, the first generation lithium batteries, first generation lithium rechargeable batteries had this problem that when we buy the battery knew it will be fine, and you keep using it for several cycles you know whatever 10 cycles or something 10, 15, 20 cycles you may not see any problem it will be working fine, because at that point this is still growing this is not completed the short circuit, it will keep continuing into function suddenly one day you have the short circuit. So, suddenly one day you end up in the situation that there’s a short circuit.

That time almost immediately the battery will explode. So, the first generation lithium ion batteries with that were put in the market actually used to explode, and they had all got to be recalled they became very dangerous and you know even in fact, some of the early factories of lithium batteries even caught fire. So, that the entire factory got burnt on one of the factories got burnt on into this. So, this is a problem? So, this was a problem, but incidentally this is not a problem with single use batteries.

So, single used lithium batteries didn’t have this problem because you never plated it back only when you plate this back you have the dendritic structure growing, which can continue to grow and make the short circuit. So, it was not an issue with lithium single used batteries or non rechargeable batteries, but it was a problem with lithium rechargeable batteries and this was primarily, because the there was a plating, stripping mechanism.

And this plating process was creating the situation, therefore; they decided that using lithium metal as the anode was not a safe thing to do because that required this plating and removal kind of thing. So, instead of doing putting lithium metal they started to look for other materials which are then called as host materials, inside which lithium can sit at a potential very close to the lithium metal potential. So, now, the lithium is not sitting in the front surface, it is actually going into the structure and sitting inside that structure, and then when you discharged the cell is coming out from the structure going to complete the reaction when you recharge again it goes back into the structure ok.

So, it is not on the surface it goes inside the structure. So, that kind of a host material began to be used as the anode as suppose to lithium. And in that case you never have lithium as metal form, you only have it in ionic form and that is why the new generation batteries are called lithium ion batteries the lithium sort of stays ionic throughout the circumstances that it is presented with.

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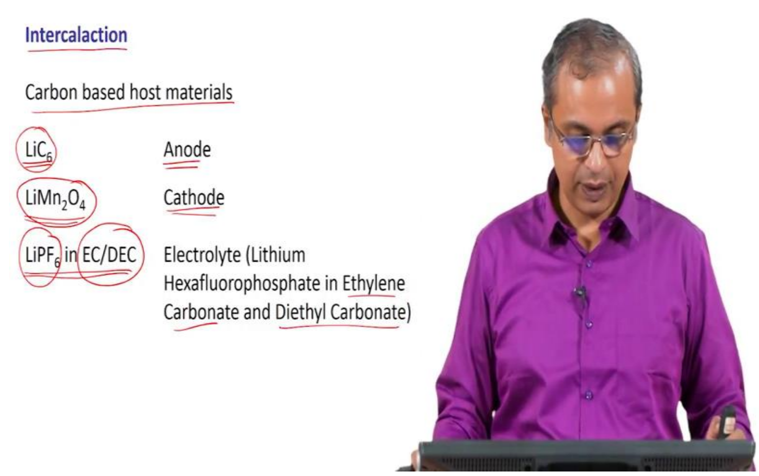

So, typically people have now used carbon based host materials for the anode and therefore, the anode is typically LiC 6 it is a combination of lithium and carbon and typically graphite is used LiC 6 is the material that is used, and in similar kind of fashion to have a lithium manganate as the cathode, that is the cathode and the electrolyte is a some salt of lithium. So, lithium hexafluorophosphate is what I am indicating that one of the combinations and that is usually put into some solvent okay and you cannot use water here because water will react with lithium.

So, you cannot use water here. So, there are some organic solvents. So, in this case it is ethylene carbonate and diethyl carbonate, but there are various other combinations dimethyl carbonate is there, with various other solvents are also been investigated and used, but it's typically a salt of lithium in some ethylene carbonate diethyl carbonate kind of thing. Lithium magnate many other cathode materials have also been investigated, primarily with intention of having high voltage window between lithium and carbon and this lithium maganet. And another set of host materials are being investing for the anode which are mostly carbon based.

So, they are looking at nano tube they are looking at graphene various different carbon based sources which can hold the lithium at the potential very close to lithium metal. So, you are not losing the potential of the lithium metal, but you are not keeping it as lithium metal. So, the plating stripping process is not there and therefore, this dendritic growth is not an issue and short circuit is not an issue.

So, this is this idea that you will keep the carbon inside a host, I mean sorry you will keep the lithium inside a host material is and given the structure of graphite which is a layered structure, this keeping of carbon inside this layered structure of graphite is referred to as intercalation that is this term called intercalation. So, when you talk about lithium batteries lithium ion batteries. Typically you will hear this term intercalation which is basically this idea that lithium is being stored within the layers of graphite and that is this idea of intercalation.

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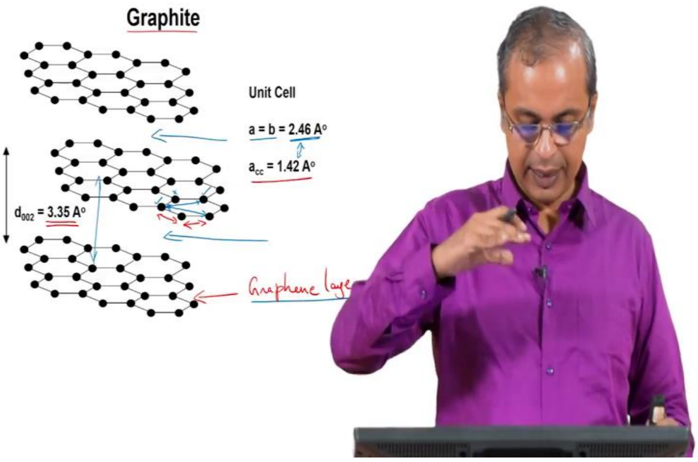

So, if you see here the graphitic structure is here and you can see that it is you know hexagonally layered I mean hexagonally bonded carbon atoms. So, you have 6 6 carbon atoms and then you have this layered structure. Each layer is referred to as a graphene layer and you have you know layered structure where this is how the layering is done and the spacing between those layers is 3.35 angstroms this is the d 002 planes these are called 002 planes if you know the crystal structure notation. If you don't know it doesn't matter you just have to remember that it's a layered structure layers of carbon atoms are present and the spacing between them is 3.35 angstroms.

The carbon-carbon bond length is 1.42 angstroms. So, that is basically this bond length here or this bond length here, that is the carbon-carbon bond length and that is about 1.42 angstroms. The a versus I mean when you look at the crystal crystallographic you know unit cell parameters you have a equals b equals 2.46 angstroms, which is different from this 1.42 angstroms. So, that is because we are not calling the carbon-carbon bond length the convention is with respect to graphite is not to call the carbon-carbon bond length as the a axis or b axis, but rather to call this distance as you are a direction and similarly this distance would be your b direction. So, it is not the immediate next neighbor, but the neighbor after that.

So, it is not it is not this one, but this one. If if this is your origin then it is not this first neighbor, but the second neighbor that you are accessing and that that distance is the a a or b unit cell vector and the d 002 spacing is the spacing between these planes right. So, from here to wherever that says that that spacing is your d 002 spacing. So, that is the structure. So, you have a layered structure. So, actually what can happen is, you can have material that comes in between these layers and the right kind of circumstances you can have something that enters this structure ok and this idea that you have something entering the structure in this case lithium entering the structure is called lithium intercalation.

So, you will refer to that as lithium intercalated graphite ok. So, or graphite integrated by lithium. So, that is the thing; this graphene layer as I said is the originally this is how they used to define graphene layer, it's a single layer of this graphite structure. So, graphite has all these graphene layers stacked one on top of the other or today when you hear a lot about the research of on grapheme, all though originally it was a single layer of these carbon atoms today actually they look at a few layers of carbon atoms together, which is represented as the graphene they are looking more to see what is the level of disorder in the structure, and then as long as it stays above a certain level of disorder they would still like to classify as graphene based on the electronic structure as well.

So, there are some other parameters they look at before they call it graphene. So, it's not necessarily single layer graphene that you hear about when you when they talk about graphene in the literature, you can have multiple layers and that's the context in which you have to understand it, so anyway. So, this is the way in which a lithium can enter it enter the structure and that is lithium intercalated graphite.

It is interestingly when lithium enters graphite as a host material, certain interesting phenomena happen and so, this intercalation process is what we will look at very briefly here, here we have a range of graphene planes. So, I am just keeping them now parallel to the each other and if you are looking at them a side on; so, here we are looking at a little bit from an angle. So, that's why we are able to see the carbon atoms, a instead of this I am just looking at layers of the graphine structure; graphite structure directly you know such that the layers are in line with us or the perpendicular to the layer is exactly you know parallel to us.

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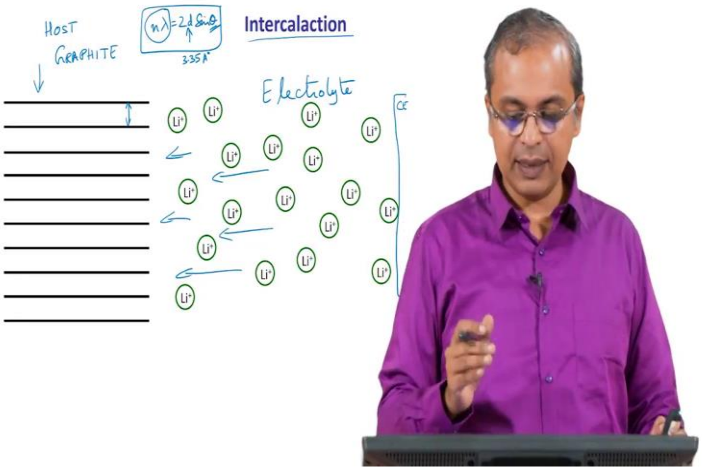

So, we are looking at it from sideways. So, to speak and this is the electrolyte. So, this is the host graphite, and this is the electrolyte. So, from here with time if you put if apply let's say your recharging the material. So, right now there is no lithium sitting inside graphic that is absolutely no lithium sitting inside the graphite now if you do recharging. So, we have some counter electrode. So, that counter electrode I am not showing you here it is outside the scope of this drawing, its outside this drawing.

So, we just assume that is a counter electrode sitting somewhere there, and from there lithium ions are coming. So, we just called this as a counter electrode. So, lithium ions are moving this way ok. So, interestingly what happens is, they don't just randomly enter this graphite structure, they do so, in some kind of a periodic manner one very periodic systematic manner in which they enter this graphite structure is been noticed, and that is referred to as staging it. And lithium enters graphite in stages and the process is referred to as staging and what happens is there are like a stage 4, stage 3, stage 2 and stage 1 kind of situation that arises in this process, I mean reach stage one only you have reached the complete you know completion of the reaction and you have Li C 6 at that point okay.

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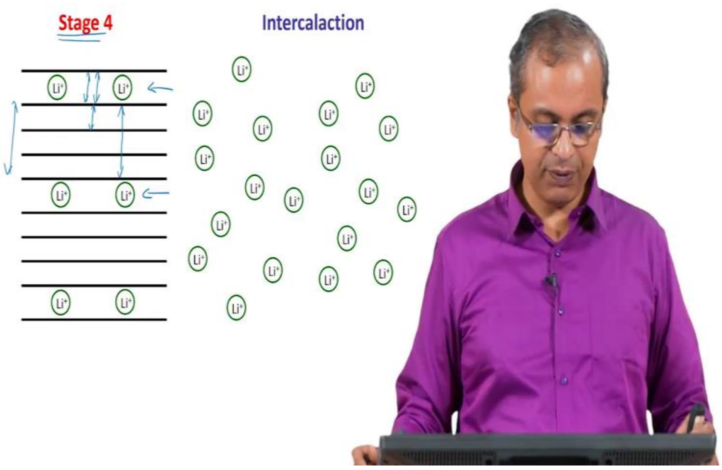

So, what happens for example, when you do this, you will notice this is the first this is the stage 4 this is called stage 4. So, it is happening in reverse, stage 4 simply refers to this idea that there are 4 layers of graphene between two adjacent layers of lithium ions that have intercalated into the system.

So, lithium ions have intercalated into the system. So, between two adjacent layers of lithium ions, you have 4 layers of graphene and so okay, this is how. So, what I will also point out that, you see here the spacing has gone up this spacing is the little larger than this spacing that is because the ions are coming there. So, ions have come in there there is a lot of study and I know exactly what is the status of lithium there, how much of the electron is with it, how much of the electron is with the rest of the host material etcetera.

So, for our purpose we will simply call it the lithium ion that is there. So, lithium ion has come in there and then it has increased the spacing between graphene layers where it is present, but these spacings are undisturbed right. So, this is the original spacing. So, if you compare again with the previous picture, this is how our picture was and you have some variation the electrolyte also because ions are moving. So, you can see the ions if you look at the electrolytes side ions are moving. If you look at the electrode side the spacing has changed, you had uniformly spaced graphene layers and you find now that some of the graphene layers have been pride a part, have been pushed apart and some of them continue to remain as per their original spacing and you have this lithium that has come inside it.

So, this is stage 4; stage 3 as you can imagine with respect to this description, would be a situation where we brought in a so, much lithium that on average there are three graphene layers between two lithium layers. Now, you are 4 graphene layers between two lithium layers, we introduce more lithium as they grow go inside and inside they will readjust such that they are now you have 3 graphene layers between two lithium layer. So, so this situation evolves into this situation.

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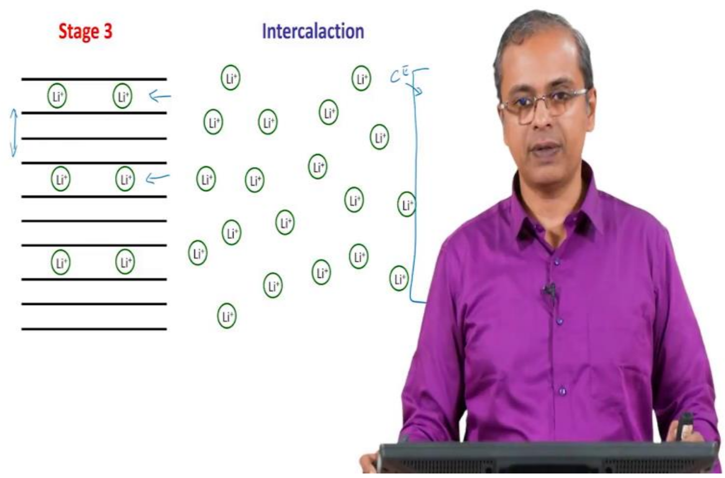

So, suddenly you now have three layers only between every two adjacent graphene layers. Again electrolyte is continuing to change here and you continue to have a counter electrode here from where this is happening. So, this is what this is ok. So, this is 4 layered 4 layers of graphene between two lithium layers this is 3 layers of graphene between two lithium layers. So, this is stage 3.

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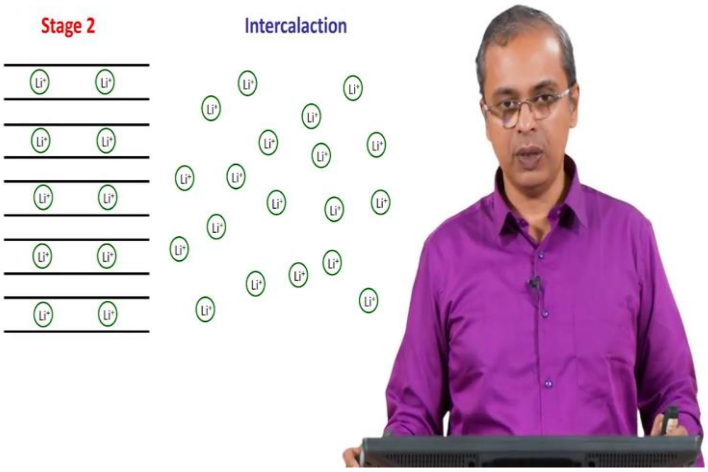

We can continue this and you will have stage 2 where you have two layers of graphene between two adjacent lithium layers.

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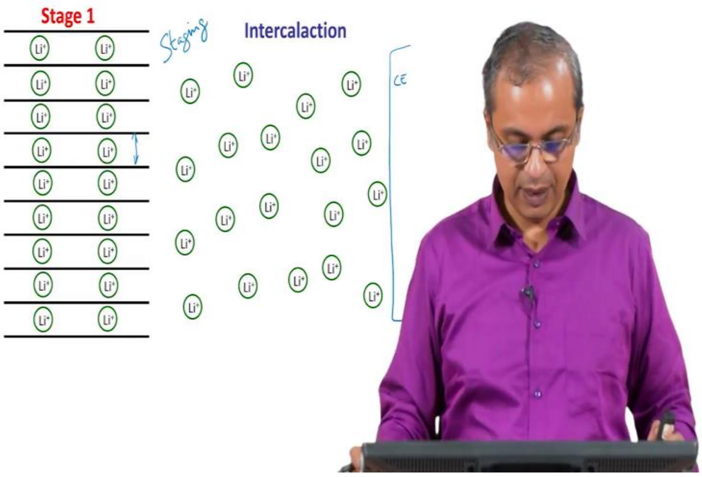

And then you have stage 1, where you have all the graphene layers intercalated with lithium layers lithium ions. So, these are all the stages. So, when you discharge also it will do the opposite. So, if I am if this is the charged condition and start discharging the cell it will go like this. Now all the lithium is gone to the counter electrode, you recharge it will do this ok. So, this is how the charging and discharging happens. So, this is fully charged discharging, discharging, discharging, discharging fully discharged then recharge.

So, this is fully recharged. So, this is how charging discharging happens and in this process there is no plating of lithium here this is not happening, there is no plating here and therefore, the lithium is safe this idea of dendritic growth is not happening, it is not growing such that you will have a short circuit, so all that is not happening. So, this safety issue which was there with the lithium metal is no longer there ok. So, I will also point out that you can see here that the spacing has changed. You can see if you compare this spacing here, it is significantly higher than the original spacing between the graphene layers which is this.

So, therefore, when you do x ray diffraction of the cell, you will find that this initial spacing that you know we had this 002 spacing of 3.35 angstroms. So, when you do x ray diffraction of this, if you do n lambda equals 2 d sin theta which is the Bragg equation right. So, this is the Bragg equation. So, this d is 3.35 angstroms. So, if you use a particular value of wave length, you will get a particular theta at which the peak will show up right. So, now, as you put lithium into it on average the spacing is increasing on average the spacing is increasing right. So, in other words on average the d value is going up on average the d value is going up. So, as the d value keeps going up, the theta at which the peak will appear keeps decreasing. Because 2 d sin theta has to be a constant n lambda is a constant you are using the same wavelength.

So, lambda is the constant. So, if you keep increasing the d theta has to come down. So, the peak the position of the peak that angle at which the peak appears the XRD peak appears will keep shifting to lower values of theta. So, it will shift to a lower value of theta and you will see the peak appearing at lower and lower values and in fact, this is a clearly been observed, you can do experiments you can do you know in situ x ray diffraction kind of experiment were you have a lithium cell inside the x ray set up, and you can run the cell, and then you can see this you know steadily the d 002 two peak shifting to lower and lower values of theta. So, that is what happens and this idea that, it happens in stages is referred to as staging.

This is called staging. So, intercalation happens through this process of staging in graphite and it helps secure the lithium in a safe way and it helps create a situation where the lithium ion battery can function safely. So, that is I think is a very key part of this whole lithium ion technology. So, we saw what are the advantages of lithium battery, we saw what are the hazards with the lithium ion with the lithium battery. So, advantages of the lithium the you know hazards associated with the lithium battery and what is the process that they have followed to overcome that hazard, which has created the lithium ion battery and this is the battery that is the prevalent in a large scale in our current usage. This is the technology this exact same thing that I am showing you here is basically the idea that people have used to create the lithium ion batteries that we are presently using.

I will also point out that you know this is using graphite as the material, you can use other forms of carbon also and in fact, people actively look at other forms of carbon to do this same process and so, there is lot of research that goes on in this area.

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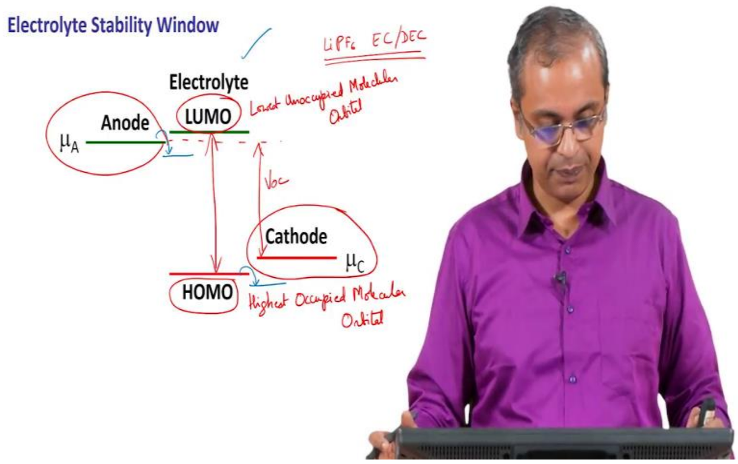

Incidentally we should also understand what is the relationship between the electrolyte, what is being required of the electrolyte and what is being required of the electrode and how do those two relate to each other. We spoke about a specific case where you know you had the lithium we had Lithium Hexafluorophosphate right LiPF 6 and that we had with some solvent EC DEC some some combination like this, which was being used as the electrolyte how did you select this how do we select this, right.

So, to do that, we have to actually understand something about the energetics of of that electrolyte. So, we have something called the highest occupied molecular orbital or HOMO it is called highest occupied molecular orbital and this is the lowest unoccupied molecular orbital, this gap is very important. In an electrolyte you will have this HOMO HOMO and LUMO these are the two terms that are used, the highest occupied molecular orbital and the lowest unoccupied molecular orbital, the Fermi energies or the chemical potentials of the anode and cathode, chemical potential of the anode and the chemical potential of the cathode should be selected should be matched with the voltage window of the permissible voltage window for the electrolyte.

This gap in energy between the HOMO and the LUMO is the permissible energy window for that electrolyte. So, as you can see here, if you look at the anode and cathode this is the gap between anode and cathode, this is the open circuit voltage. This is the open circuit voltage between the anode and cathode and it stays within the voltage window of the electrolyte the HOMO LUMO window that you see here, this anode cathode window should stay within that, only then this system will work in a stable manner why does why is this the case? It is because at the anode during the normal discharge process when you use the battery, the anode material is getting oxidized right.

So, it is releasing electrons. Now if the LUMO of the lowest unoccupied molecular orbital of the electrolyte, if it were to be lower let’s say it were here, then this electron can directly go to the LUMO itself in which case the anode is actually reacting with the electrolyte it is reducing the electrolyte the anode is getting oxidized, but instead of releasing the electron to the external circuit it is actually releasing the electron to the electrolyte and the electrolyte itself is getting reduced.

And similarly if the if the cathode were lower here in the cathode as the cathode gets reduced, it will take the electrode electron from the electrolyte. So now, instead of having electrons being released to the external circuit, they will get consumed by electrolyte itself it based on the position of the electrode right. So, you will the electrode reacting with the electrolyte and that will basically spoil the cell, you will not get energy out of the cell. And therefore, this is not something that is desired. So, we basically want a situation where this window between the anode and cathode stays within the window of the HOMO and LUMO of the electrolyte, it’s not outside of this window of the HOMO and LUMO of the electrolyte ok.

So, that is the way in which we match the operating potentials of the anode cathode with the operating voltage window of the electrolyte. And this is true not only for the lithium ion system it is true for all the electrolyte electrode combinations that you may see in any other battery system.

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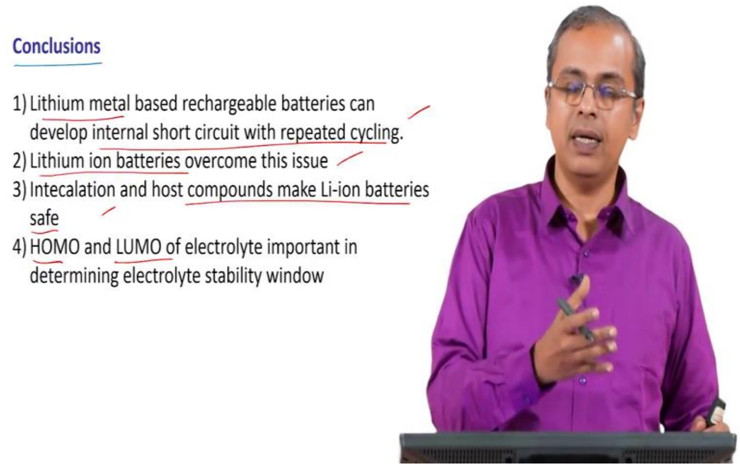

So, in terms of conclusions, our main conclusions are that the lithium metal based rechargeable batteries can develop internal short circuit with repeated cycling. So, we saw first of all that the there are huge advantages to using the lithium metal based battery system, and that is why there is so much interest in it, but you also so, noted that if you use lithium metal as the anode, then you can have internal short circuit with repeated cycling and that is a not desirable situation to have.

The lithium ion based technology creates a situation, where metal is not being plated and stripped. And therefore, the dendritic structure which is the danger that happens dangerous situation that happens in the lithium metal based system, that dendritic structure does not grow in the case of lithium ion batteries of course, you have to some mass balance here to ensure that you are not putting excess lithium into the electrode. If you put excess lithium then eventually you can have dendritic growth there also.

So, they do some careful mass balancing to ensure that lithium is exhausted, but there is still little excess carbon available right. Because Li C 6 will form, you should not have more lithium than that if you send more lithium than that lithium will start plating on top of graphite, we don't want that we will just keep little less lithium than possible to be held within that graphite.

I mean that in the basis we overcome this plating issue. Intercalation and host compounds make lithium ion battery safe. So, that is the idea that we explored in some detail and we also saw that it is very important to match the operating you know allowed operating window of the electrolyte with the energy values associated with the anode and cathode of the battery only when you do that the system is actually safe. And only then you will actually get current meaningfully out of the battery, otherwise you will have the electrodes reacting with the electrolyte which is a completely understandable situation. And you are actually wasting the electrode you are also wasting the electrolyte, you won't get any current at the external circuit.

So, that is our main conclusions for this class on lithium ion batteries. And as I said this is a very important technology in today's world of you know portable energy, lot of research course on it. And this is what we discussed today is many of the basic concepts associated with this lithium ion battery technology.

Thank you.

KEYWORDS:

Lithium Ion Batteries; Lithium Metal based Battery; Lithium Ion based Battery; Lithium Ion Technology; Intercalation; Solid Electrolyte Interface Layer; Dendritic Growth; Internal Short Circuit; Battery Explosion; Ion Conductivity; Electron Conductivity; Thermal Runway; Lithium single used batteries; Non Rechargeable Batteries; Lithium Rechargeable Batteries; Plating Stripping Mechanism; Host Material; LiC 6; Lithium Manganate; Lithium Carbon Host Material; Lithium Hexafluorophosphate; Ethylene Carbonate ; Diethyl Carbonate; Dimethyl Carbonate; Graphite; Lithium Intercalation; Lithium Intercalated Graphite; Staging; Highest Occupied Molecular Orbital (HOMO); Lowest Unoccupied Molecular Orbital (LUMO)

LECTURE:

Lithium Metal batteries and Lithium Ion batteries are explained in detail. The pros of Lithium Ion batteries over Lithium metal batteries is listed. Concepts of plating and stripping, and a mechanism called intercalation to overcome plating and stripping is discussed.