Electrochemical Energy Storage
Prof. Subhasish Basu Majumder
Department of Materials Science Centre
Indian Institute of Technology, Kharagpur

Module - 07
Introduction to battery pack design
Lecture - 32
Degradation and Safety Issues of Li ion Rechargeable Cells

Welcome to my course Electrochemical Energy Storage and this is module number 7, where I am discussing the Introduction to battery pack design. And this is lecture number 32, where I will be talking on Degradation and Safety Issues of Lithium ion Rechargeable Cells.

(Refer Slide Time: 00:53)

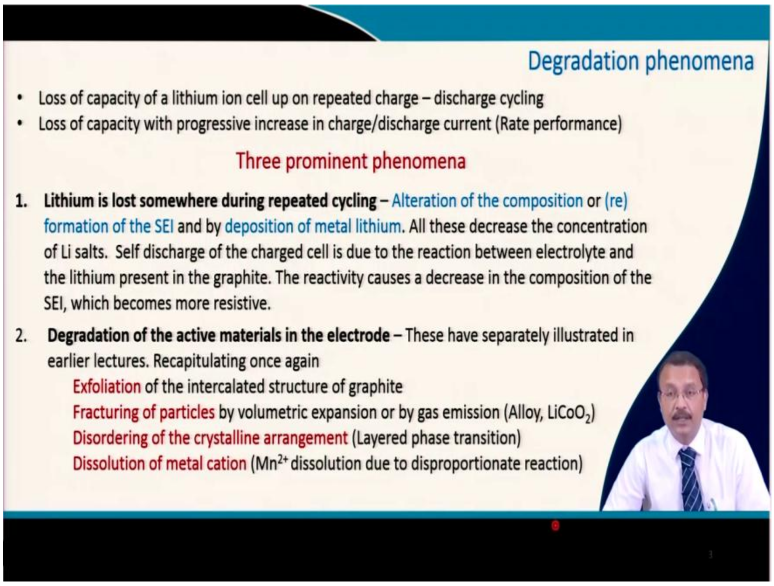
CONCEPTS COVERED

- Degradation phenomena
- Operational safety
- Transport and storage of lithium ion batteries

Now first I will talk, in fact this is some kind of recapitulation, you already know about it; but this is important to know the degradation phenomena of each individual cell. Because now what we I am trying to do, is to connect it in series and parallel to make a battery module.

And the degradation is important, because if the cells are degraded during its operation, their cause is not known then you cannot take the precautionary step, so that you cannot take the precautionary step to built a bigger and quality battery. So, the operational safety is also important. So, we will also talk about it and how to transport and store this individual cell or battery modules that will also be introduced.

(Refer Slide Time: 01:58)



Degradation phenomena

- Loss of capacity of a lithium ion cell up on repeated charge – discharge cycling
- Loss of capacity with progressive increase in charge/discharge current (Rate performance)

Three prominent phenomena

1. **Lithium is lost somewhere during repeated cycling** – Alteration of the composition or (re) formation of the SEI and by deposition of metal lithium. All these decrease the concentration of Li salts. Self discharge of the charged cell is due to the reaction between electrolyte and the lithium present in the graphite. The reactivity causes a decrease in the composition of the SEI, which becomes more resistive.
2. **Degradation of the active materials in the electrode** – These have separately illustrated in earlier lectures. Recapitulating once again
    - Exfoliation of the intercalated structure of graphite
    - Fracturing of particles by volumetric expansion or by gas emission (Alloy, $LiCoO_2$)
    - Disordering of the crystalline arrangement (Layered phase transition)
    - Dissolution of metal cation (Mn^{2+} dissolution due to disproportionate reaction)

So, degradation basically is the loss of lithium somehow in the cell on repeated charge and discharge cycling. So, this is considered the cyclability. And also the capacity can be lost with progressive increase in charge and discharge current. So, that is very relevant for electric vehicle use, it is not a continuous discharge; sometimes it is a continuous discharge, sometimes you are discharging at a very low rate, sometimes you are discharging at a very high rate.

So, there is a change in the rate current and the capacity is also affected with the change in the rate current. So, this two basically degrades the cell performance. Now, there are three prominent phenomena which is responsible for this; the first one is lithium is lost somewhere during repeated cycling. So, alteration of the composition or reformation of the SEI layer and by deposition of metal lithium, these three are the root cause.

Alteration of the composite means that, in the virgin state, the positive electrode is having a particular structure; then you are extracting the lithium during charging and then during discharge, this lithium is again going back to the host lattice. But when they are going back to the host lattice, it is not same like the virgin lattice where from they came.

So, there is a structural transition is taking place, layer structure can be transformed into a spinel structure or there could be this P 2 to O 3 to P 1 this kind of transition which is relevant for the oxygen packing that is taking place. So, that environment is completely change and you cannot expect that the lithium will exactly go back and sit in the respective position the way it were in the one virgin state. And that will certainly lead to poor coulombic efficiency.

Second one is SEI layer formation. So, some part of the lithium is lost in the negative electrode part, because of the formation of the SEI. And in most of the instances this SEI is basically pervious to the lithium ion movement; because that is a decomposition product of the electrolyte, so lithium can pass through.

But when the SEI is thicker because of their poor mechanical integrity with the anode material; then what will happen, you will find that the lithium is lost. And finally, at low temperature as well as when the rate of charge is too high, electroplating of lithium on the anode surface can also be possible, followed by dendritic formation and lost of this lithium into the electrolyte, because of the disintegration of this kind of your lithium deposition.

So, all those create the lost of lithium. So, this basically decrease the concentration of lithium salt. And self-discharge of the charge state is due to the reaction between the electrolyte and the lithium present in the graphite. So, that is also one cause where in the charge state when all the lithium is present in the graphite, it start to react with the electrolyte.

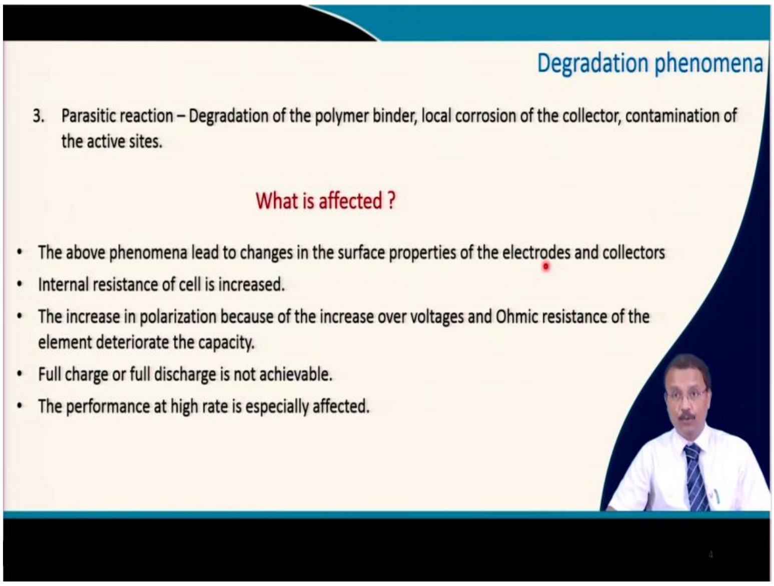
And this reactivity causes a decrease in the composition of the SEI and it becomes more resistive for the effective charge transfer. So, the charge transfer resistance from the Nyquist plot, you will see that it is enhanced, increased. Second one is the degradation of the active material in the electrode. This I have separately illustrated in earlier lectures, I have already talked about it.

Exfoliation of the intercalated structure of the graphite, so that breaks the layer of the graphite; then fracturing of particle by volumetric expansion or by gas emission, this is pertinent to metal alloy and also lithium cobalt oxide this gas emission and also the lithium manganese rich positive electrode material, the oxygen evolution takes place during charging beyond 4.5 volt.

Then disordering of the crystal arrangement, so, layered phase transition that also I talked about. So, that all these things degrade the active materials in the electrode. And finally, the dissolution of metal cation under certain circumstances manganese 2 plus if it is present it dissolves in the electrolyte due to a disproportionate reaction, manganese 4 plus and manganese 3 plus.

So, there is a disproportionate reaction and it basically; if manganese 3 plus is affluent, it causes manganese 4 plus and manganese 2 plus ions and manganese 2 plus dissolute inside the electrolyte, so that degrades the active material in the respective electrode.

(Refer Slide Time: 08:17)



Degradation phenomena

3. Parasitic reaction – Degradation of the polymer binder, local corrosion of the collector, contamination of the active sites.

What is affected ?

- The above phenomena lead to changes in the surface properties of the electrodes and collectors
- Internal resistance of cell is increased.
- The increase in polarization because of the increase over voltages and Ohmic resistance of the element deteriorate the capacity.
- Full charge or full discharge is not achievable.
- The performance at high rate is especially affected.

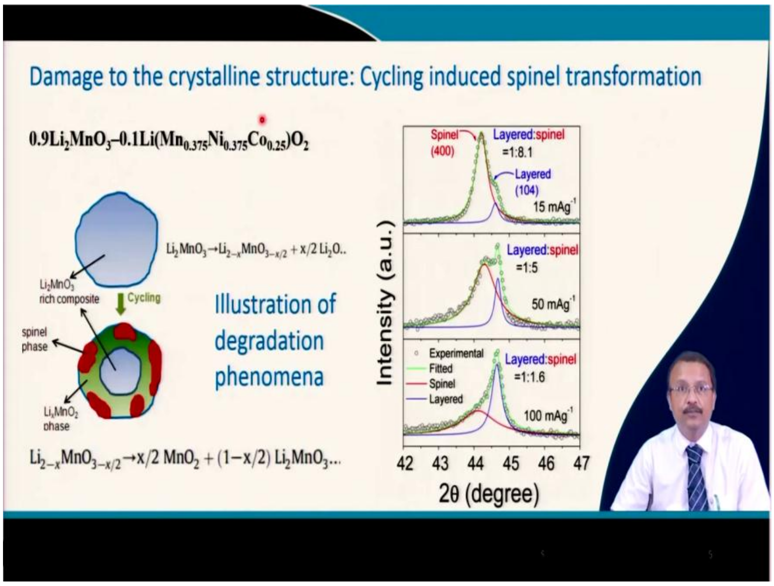
Apart from that there is a parasitic reaction, so that degradation of the polymer binder is possible. So, that will disintegrate the whole composite electrode material. Local corrosion is possible with the collectors, particularly if stress amount of water is there. So, HF will be generated and this hydrofluoric acid will corrode the current collector and contamination of the active sites that is possible, where lithium go and set.

So, these are the root causes of the degradation and what exactly is affected due to this? So, this phenomena lead to the change in the surface property of the electrode and also the current collectors. Internal resistance of the cell is increased, so that will lead to the problem of cell balancing, which I was mentioning in the last lecture.

The increase in polarization because of increase of over voltage and Ohmic resistance of the element deteriorate the capacity. Then full charge or full discharge is not achievable, because of this degradation phenomena; the performance at high rate is especially affected.

So, all this factor, this degradation and the factors that is being affected due to those cell degradation that, basically is of major concern because of the cell balancing will become progressively more and more challenging, that is why it is very important to get the cell of equal kind of or the homogeneous kind of electrochemical performance, rather than some cells they are performing well, some cells are really bad, some cells are moderate and then cell balancing will be really really problematic.

(Refer Slide Time: 10:25)



Damage to the crystalline structure: Cycling induced spinel transformation

$0.9Li_2MnO_3–0.1Li(Mn_{0.375}Ni_{0.375}Co_{0.25})O_2$

$Li_2MnO_3 \rightarrow Li_{2-x}MnO_{3-x/2} + x/2\ Li_2O$..

Illustration of degradation phenomena

$Li_{2-x}MnO_{3-x/2} \rightarrow x/2\ MnO_2 + (1-x/2)\ Li_2MnO_3$...

So, the damage of the crystalline structure one example I have shown it here. And this is very important for this type of LMR kind of cathode, lithium and manganese rich cathode material, which I introduced earlier. You know that during charging from this phase L i 2 M n O 3, this phase an oxygen comes out and basically it forms a L i; after once you take out this L i 2 O lithium and oxygen, oxygen is coming out along with the lithium and it forms a structure like this and when all the lithium is you are taking out, you get a M n O 2 structure.

So, when you discharge it, then this M n O 2 it is free to take lithium. So, basically it forms lithium manganese oxide phase. So, now, this lithium manganese phase upon repeated cycling what will happen that, this manganese oxide will take lithium and remaining part is still Li 2 Mn O 3.

So, you can see that Li 2 Mn O 3 was there, it is still there; but part of it, it was transformed to manganese dioxide and then upon lithiation during the next discharge cycle, it forms this Li x Mn O 2 type of phase. So, there are three different types of phase right, sorry two different types of phase; one is this unreacted or yet to be reacted lithium manganese oxide and this is from the created manganese oxide upon intercalation of lithium, you get this phase Li Mn O 2 type of phase electrochemically prepared.

Now, once you start to cycle it, you will find that this structure will be structurally transformed into a spinel phase; something like a b 2 o 4 kind of Li Mn 2 O 4 kind of phase. And this layer to spinel phase transition in this LMR cathode, that is detrimental for their cyclability. So, cyclic characteristics will be deteriorated.

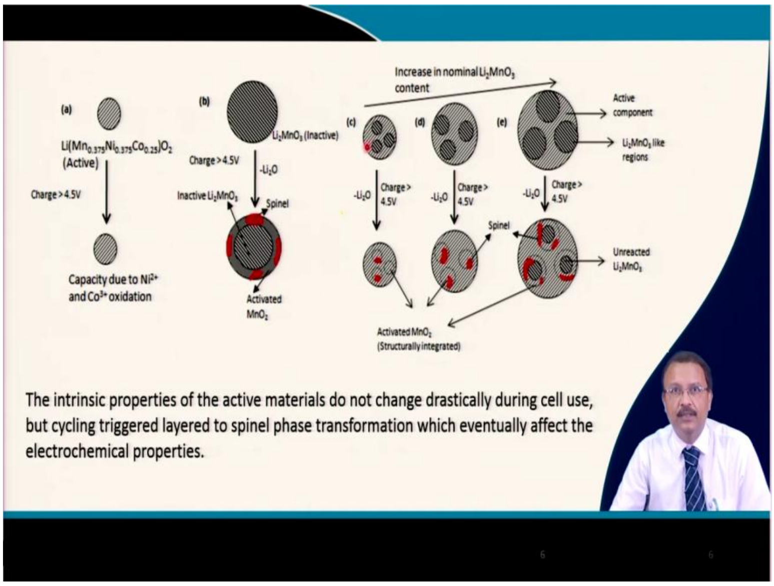
Now this can be identified by the X ray diffraction study. So, you can see that the spinel phase is there along with the layered phase at certain level of cycling of this particular cathode. And from this peak area, you can calculate what is the actual volume content of spinel and the layered material. And you can find that when you are charge and discharge at relatively low rate, here in this case 15 milli Ampere per gram; then if this layer to spinel transformation is very high 1 is to 8.1.

So, once you are cycling it at relatively low rate, then this spinel to sorry layer to spinel phase transition is expedite. Progressively once you increase this current, here it is 15, then you increase it to 50, then you have increased it to further higher rate, it is 100 milli ampere per gram; then progressively this layered phase transition, layer to spinel phase transition is progressively reduced. You see at higher rate, this transformation is grossly retarded.

So, it is a boon, instead of reducing the capacity, we will find the capacity is in fact increase when you cycle it at higher rate. So, this kind of structural change that happens while you charge and discharge at different rate for various chemistry we have discussed for lithium as well as sodium ion battery, that is very important; because you will have to do lot of study, just to understand that at which state what is happening.

And you will have to gain insight from the materials point of view; from its structural and micro structural point of view that, what is the root cause of this kind of variation. So, it is exactly opposite way that usually we find. We find that if you increase the rate, if you drain lithium too fast or try to intercalate lithium too fast; then capacity actually reduces. But in this type of cathode, you will find the rivers; when you the rate performance when you increase the rate, then in fact its capacity deterioration is less. So, that is one part is quite interesting.

(Refer Slide Time: 15:54)



The intrinsic properties of the active materials do not change drastically during cell use, but cycling triggered layered to spinel phase transformation which eventually affect the electrochemical properties.

So, we try to show you that, this is the phenomena that already I talked about. So, this is the active material and once you charge more than 4.5 Volt; then basically all the capacity is due to nickel as well as cobalt this type of oxidation. Then along with that, this inert part lithium manganese oxide which is inactive, so that yield this layer to spinel transformation. And this layer to spinel transformation basically one can retard, if you have the rating, this cycling rate at higher current.

So, it is a very complicated phenomena where you can understand that, you can change the content of this L i 2 M n O 3. In the last slide if you remember that, here we have used a very high percentage of this inactive phase and the active phase was only 10 percent. So, I have the flexibility to change this, to increase it and reduce it.

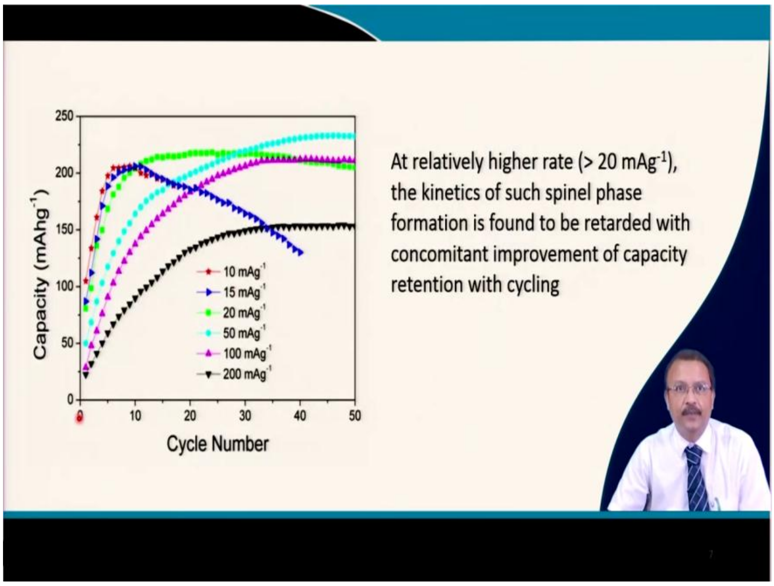
So, this part is important that, inactive part is almost 90 percent. So, in the next view slide I have shown that, increase of the nominal L i 2 M n O 3 content; you see here the M n O through content is pretty less, then the spinel transformation is also relatively less. But once you increase this content progressively higher, then you will find this spinel transformation is also high.

Now, once the spinel transformation is high in this those type of cathode; if you increase the rate, it is found that the degradation is very very marginal. So, that is one thing that I wanted to point it out that, there are lot of material science issue in designing a good cathode material and in fact, a good quality of cell. And this kind of concept is very important; the understanding that why it is happening, that is very very important for you to prepare good quality cell.

And as you can understand by now after listening all this lecture that, everything depends on material science, the quality of the cell; remaining part are all manageable, how to connect it in series and parallel, then design a b m s, then design its thermal management issue, pack it properly to have a built.

But the basic cell performance will be decided by the materials; by the positive material, by the electrolyte, by the negative material, by the current collector, along with the self fabrication how quality cells you can make. So, the material issue is very very important.

(Refer Slide Time: 19:09)



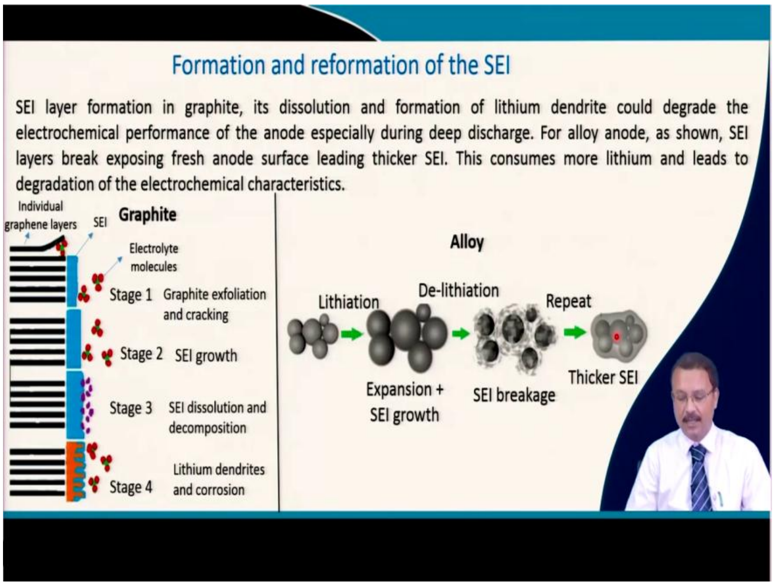
At relatively higher rate (> 20 mAg^{-1}), the kinetics of such spinel phase formation is found to be retarded with concomitant improvement of capacity retention with cycling

So, this is highlighted in this. So, if you see that progressively you are increasing the rate. So, once you have a low rate like this, there is a fall in capacity and for initial few cycles, always the capacity increases and that is related to the fact that not at one go, all Li 2 Mn O 3 is transformed to activated manganese oxide that takes part in taking the lithium and integrate into the LMR based cathode. So, it takes time.

So, therefore, it is progressively the reaction takes place, the very first slides what I showed you; you see that this is going like this and after repeated cycling all this part of Li 2 Mn O 3 that will transform into activated manganese oxide, which will eventually react with lithium to form a layer structure material, which are structurally integrated to this type of cathode.

So, for this one that is why instead of the capacity being reduced with the cycle the capacity increases with the cycle and as you can see once you cross this limit of 20 milli ampere per gram using the rate current; you see that there is no change of this kind of fall, because of the layer to spinel transition. So, layer to spinel transition is grossly retarded when you do not give it enough chance, because you are using a very high rate current. So, that is the fundamentals of the structural degradation for LMR type of cathode material.

(Refer Slide Time: 21:03)



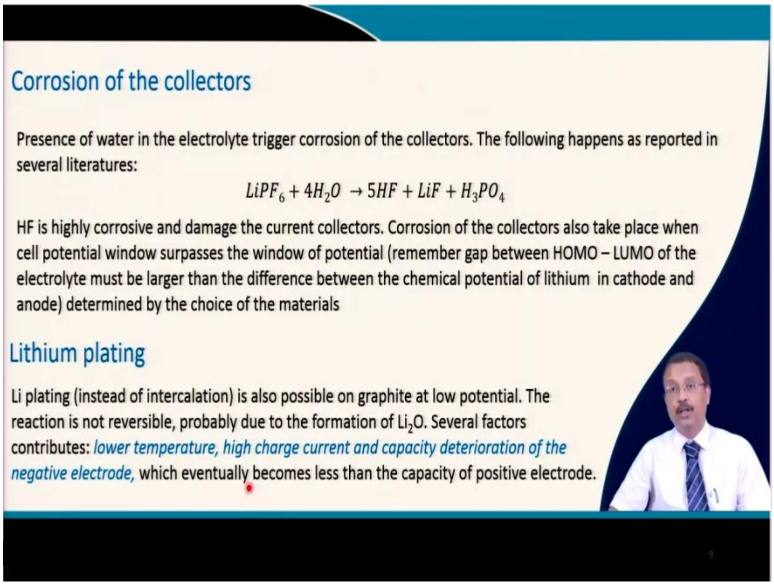
Formation and reformation of the SEI

SEI layer formation in graphite, its dissolution and formation of lithium dendrite could degrade the electrochemical performance of the anode especially during deep discharge. For alloy anode, as shown, SEI layers break exposing fresh anode surface leading thicker SEI. This consumes more lithium and leads to degradation of the electrochemical characteristics.

Formation and reformation of SEI already I have talked about. So, this is just a recapitulation that, sometime you have this exfoliation or cracking can take place, SEI growth can take place, then SEI dissolution can take place. And then if a lower surface, I mean the active surface is available; then lithium dendrite can form, that also depends on temperature as well as the rate of the charge that will expedite this dendrite.

So, all that this phenomena they eventually degrade the material; for alloy based material, it is expansion and SEI growth, then the disintegration of SEI growth, even disintegration of this particles, then delamination of the active particles from the current collector, forming a thicker SEI which is impervious to alkali ions, they all basically re degrade the cell.

(Refer Slide Time: 22:14)



Corrosion of the collectors

Presence of water in the electrolyte trigger corrosion of the collectors. The following happens as reported in several literatures:

$$LiPF_6 + 4H_2O \rightarrow 5HF + LiF + H_3PO_4$$

HF is highly corrosive and damage the current collectors. Corrosion of the collectors also take place when cell potential window surpasses the window of potential (remember gap between HOMO – LUMO of the electrolyte must be larger than the difference between the chemical potential of lithium in cathode and anode) determined by the choice of the materials

Lithium plating

Li plating (instead of intercalation) is also possible on graphite at low potential. The reaction is not reversible, probably due to the formation of Li_2O. Several factors contributes: *lower temperature, high charge current and capacity deterioration of the negative electrode,* which eventually becomes less than the capacity of positive electrode.

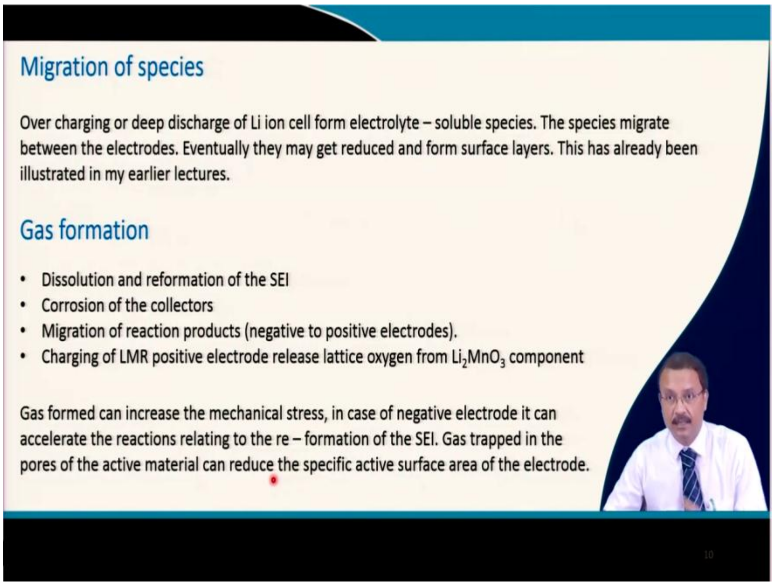
Corrosion of the collector that is another point and particularly stress level of H 2 O that reacts with the Li P F 6, which is a fluoride based salt and H F is generated. And H F is extremely corrosive and that can damage the current collectors and corrosion of the collectors also take place when the cell potential window surpass the window of electrolyte potential.

You remember that HOMO and LUMO gap, so your negative electrode will get affected. So, it will get reduced and electrolyte will get decomposed and precipitate on the surface to form a SEI layer. So, all these factors are important to be considered when you design a cell, particularly from material perspective.

Lithium plating is one of other problems and that is possible for graphite on lower potential and this reaction is not reversible; L i 2 O also can form, which is insulating in nature. So, low temperature or high charge current and capacity deterioration of the negative electrode; this becomes less when than the capacity of the positive electrode, which is more detrimental.

Already you have lower capacity of positive material as compared to a negative material; if somehow you start losing the negative material capacity, the full cell capacity will be severely affected.

(Refer Slide Time: 23:56)



Migration of species

Over charging or deep discharge of Li ion cell form electrolyte – soluble species. The species migrate between the electrodes. Eventually they may get reduced and form surface layers. This has already been illustrated in my earlier lectures.

Gas formation

- Dissolution and reformation of the SEI
- Corrosion of the collectors
- Migration of reaction products (negative to positive electrodes).
- Charging of LMR positive electrode release lattice oxygen from Li_2MnO_3 component

Gas formed can increase the mechanical stress, in case of negative electrode it can accelerate the reactions relating to the re – formation of the SEI. Gas trapped in the pores of the active material can reduce the specific active surface area of the electrode.

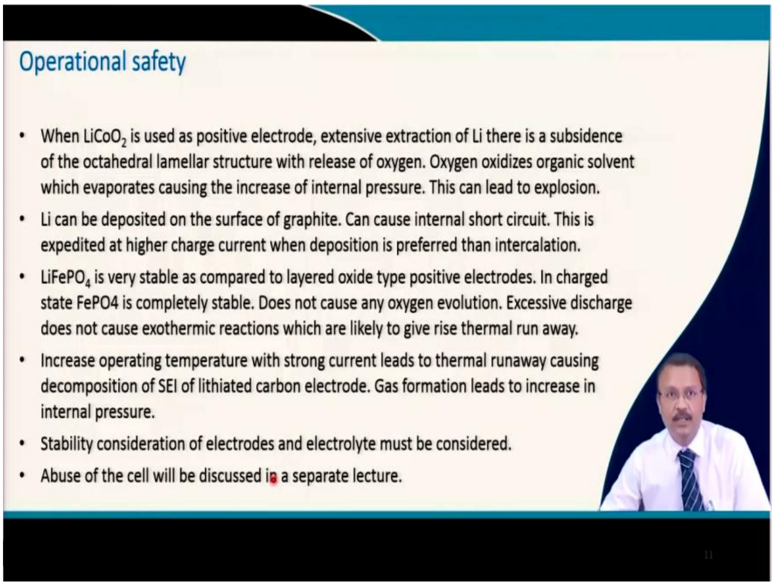
Migration of species is another factor; over charging or deep discharge of lithium ion cell form electrolyte soluble spaces. And this species migrates between the electrodes during charge discharge operation and eventually they may get reduced to form surface layer and already we have described it.

Gas formation is another problem which degrades the cell. So, this is due to dissolution and reformation of SEI one of them; then corrosion of the current collectors that also can produce gas; migration of reaction product that is another factor or charging the LMR positive cathode, this lithium manganese rich positive cathode they can evolve lattice oxygen from this L i 2 M n O 3 kind of component.

And this gas form can increase a mechanical stress. In case of the negative electrode, it can accelerate the reaction relating to the reformation of SEI. And gas is trapped in the pores of the active material and that can reduce the specific active surface area of the electrode. So, it is detrimental.

And in case of pause cell you know after forming cycle; therefore we will have to give a time, three, four cycles will have to give, so that the all the gas evolves and then you puncture it and then finally sell it. So, process complexity that is enhanced increased because of this gas evaluation.

(Refer Slide Time: 25:42)



Operational safety

- When $LiCoO_2$ is used as positive electrode, extensive extraction of Li there is a subsidence of the octahedral lamellar structure with release of oxygen. Oxygen oxidizes organic solvent which evaporates causing the increase of internal pressure. This can lead to explosion.
- Li can be deposited on the surface of graphite. Can cause internal short circuit. This is expedited at higher charge current when deposition is preferred than intercalation.
- $LiFePO_4$ is very stable as compared to layered oxide type positive electrodes. In charged state FePO4 is completely stable. Does not cause any oxygen evolution. Excessive discharge does not cause exothermic reactions which are likely to give rise thermal run away.
- Increase operating temperature with strong current leads to thermal runaway causing decomposition of SEI of lithiated carbon electrode. Gas formation leads to increase in internal pressure.
- Stability consideration of electrodes and electrolyte must be considered.
- Abuse of the cell will be discussed in a separate lecture.

Operation safety is important. You remember that lithium cobalt oxide is used under positive electrode; extensive extraction if you do of lithium, there is a substantial octahedral lamellar structure, I mean there is a change of this octahedral lamellar structure and oxygen is released.

And this oxygen eventually oxidizes the organic solvent and which evaporates causing the increase of the internal pressure because of the gas formation. And sometimes it can lead to explosion; because the reaction is exothermic and if the electrolyte is having lower flash point, then this problem exaggerated.

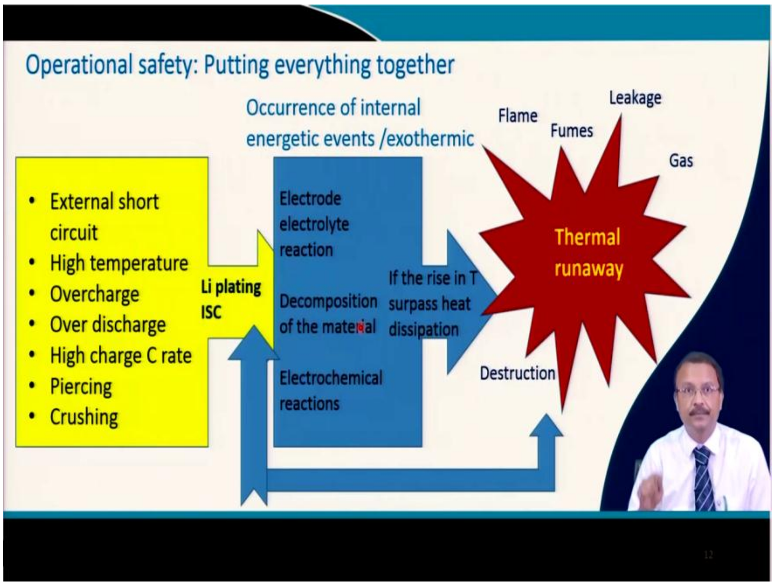
Lithium can be deposited on the graphite surface, that can cause internal short circuit; particularly at higher charge rate, it is expedited. Considering this your polyanion based material, they are very stable; that is why I like polyanion material, be that N a 3 V 2 P O 4 kind of thing NASICON structure or L i P of F e 4 they are very stable as compared to the layered oxide type of positive electrode.

And even all the lithium you take it out, your F e P O 4 is completely stable and they do not cause any kind of oxygen evaluation. And excessive discharge if you do, that also do not cause any exothermic reaction, which eventually leads to a thermal run away situation.

Increasing the operating temperature with strong current that leads to the thermal and run away and that cause the SEI to get decomposed if particularly carbon based electrode is used. And gas formation leads to increase in internal pressure. Stability consideration of electrodes and electrolyte must be considered. An abuse of the cell that, I will talk separately in as a part of another lecture.

So, I have tabulated all this operational safety, when you are selecting a particular chemistry of a cell for a particular application or you are making the cell in designing the cell choosing the right kind of positive material and electrolyte and negative material for your purpose; you should know all this material related aspect in order to form a quality cell. And that is why separately again I am recapitulating all the important aspect as far as the cell degradation is concerned.

(Refer Slide Time: 28:40)



Operational safety: Putting everything together

- External short circuit
- High temperature
- Overcharge
- Over discharge
- High charge C rate
- Piercing
- Crushing

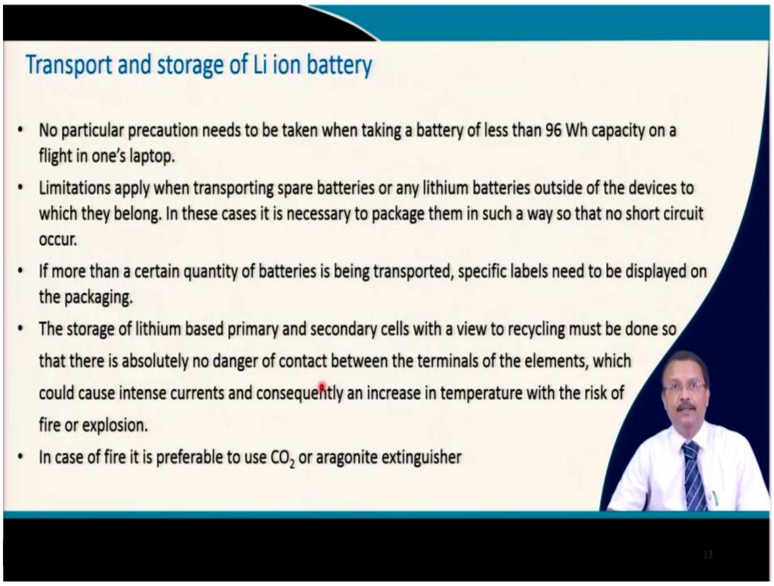
So, if you all together you put it, then these are the causes external short circuit, high temperature, over charge, over discharge, high charge C rate, I mean whatever has been specified beyond that. Piercing of the battery, you should not abuse the battery, internal short circuit will take place, crushing it.

So, handling is also important; once you use the lithium ion battery, you cannot throw it anywhere you like. So, that is extremely dangerous, proper recycling is important; another module is devoted for this purpose, so this is the reasons. And lithium plating that can lead to this internal short circuit.

And occurrence of internal energetic events that is taken place, they are all exothermic; electrode electrolyte interaction, decomposition of the material, all electrochemical reactions. Now, if the temperature rise that, surpass the heat dissipation if the thermal management is poor; if the heat whatever has been generated in a hot spot in a particular cell, there is no way it can dissipate, then what will happen, thermal run away will happen. And that will cause flame, fumes, leakage gas, and this is destruction.

So, thermal ran away is directly related to some extent to this lithium plating and internal short circuit; it is exactly when a this is quite well connected and this is very well connected if you try to pierce the battery. So, all are interrelated phenomena and this you should always keep in mind.

(Refer Slide Time: 30:29)



Transport and storage of Li ion battery

- No particular precaution needs to be taken when taking a battery of less than 96 Wh capacity on a flight in one's laptop.
- Limitations apply when transporting spare batteries or any lithium batteries outside of the devices to which they belong. In these cases it is necessary to package them in such a way so that no short circuit occur.
- If more than a certain quantity of batteries is being transported, specific labels need to be displayed on the packaging.
- The storage of lithium based primary and secondary cells with a view to recycling must be done so that there is absolutely no danger of contact between the terminals of the elements, which could cause intense currents and consequently an increase in temperature with the risk of fire or explosion.
- In case of fire it is preferable to use CO_2 or aragonite extinguisher

Transport and storage of lithium ion battery is important. Actually no particular precaution needs to be taken when taking a battery; if it is less than certain energy whatever 96, whatever that is typically the capacity of your laptop. But limitation will apply when the battery spare battery you are connecting in your hand luggage.

And there is a chance for internal short circuit positive and negative, they are connected, they are internally short circuited; then they can produce enormous exothermic reactions and that can cause fire. So, it is necessary to package them in such way, so that no short circuit is taking place. If more than a certain quantity of battery is being transported, specific level needs to be displayed in the packaging, so that people know that you should not have abuse this, it contains lithium and battery.

In fact, you from if you are importing the battery from outside, there are certain regulation in this regard. The storage of the lithium based primary as well as secondary cells is important with a view that recycling must be done, so that they are absolutely no danger of contact between the terminals of the elements.

So, that I already mentioned, you cannot throw the used lithium ion battery anywhere. So, that is extremely dangerous, even a dead battery is also extremely dangerous. In case of fire, it is preferably to use carbon dioxide or aragonite extinguisher to get rid of the fire.

(Refer Slide Time: 32:27)

REFERENCES

- **C Glaize and S Genies** " Lithium batteries and other electrochemical storage systems" Chapter – 6, page 214 – 220 Wiley, 2013 (Study Material)
- **Jung Ki Park**"Principles and Applications of Lithium Secondary Batteries" *Wiley VCH*, 2012, C
- **John Warner**" The handbook of lithium – ion battery pack design" Elsevier, 2015

So, this part of the lecture, this book it already I have referred it and there is a nice description of this book and that is your study material; apart from that, these two book are also quite informative. So, I would like you to read this two particular books.

(Refer Slide Time: 32:50)

CONCLUSION

- Degradation phenomena: Various types are explained
- Operational safety: Causes and consequences of thermal runaway are illustrated.
- Transport and storage of lithium ion batteries are discussed

So, in this particular lecture, we talked about the degradation phenomena and various types of degradation phenomena. And they are explained that what are the root cause of this degradation; then operational safety is important, what are the causes and consequences of thermal ran away, that is illustrated. And finally, the precautionary measure for transport and storage of lithium ion batteries they are discussed.

Thank you for your attention.