

Electrochemical Energy Storage
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Module - 03
Lithium batteries
Lecture - 15

Properties of Electrode Materials (Conversion Type Oxide as Case Study)

Welcome to my course Electrochemical Energy Storage and we are in module number 3, where we describe the Lithium batteries and this is lecture number 15, where Properties of Electrode Materials are being described. And earlier lecture, you know we talked about laboratory preparation of alloy based material and in this particular lecture, we will introduce Conversion Type Oxide and that is also as a Case Study.

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CONCEPTS COVERED

- Requirements of negative electrode : recapitulated
- Conversion type negative electrode : Problems associated
- Addressing the problems of negative electrodes
- Case study : Spinel zinc ferrite as conversion type negative electrode
- Electrochemical performance

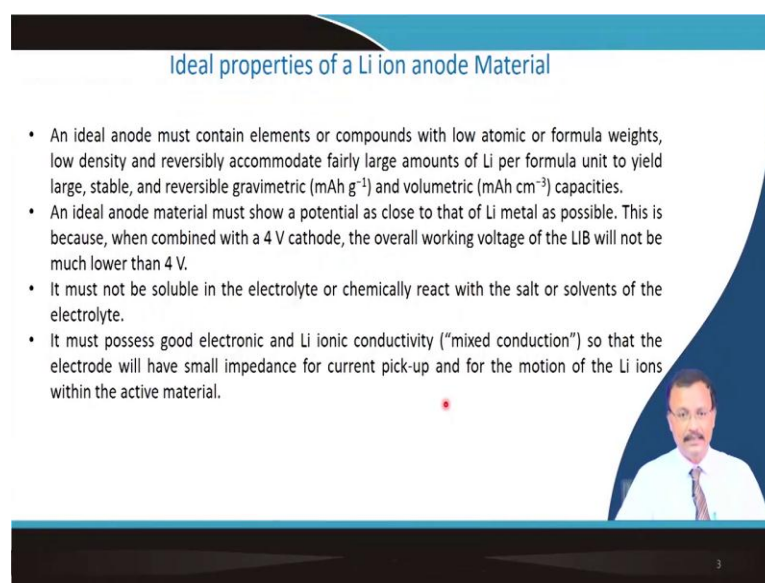
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So, the requirement of the negative electrode, again I will recapitulate. So, time and again I want to emphasize that, so that it is properly understood. Then conversion type of negative electrodes, that already I have introduced part of it and now we will see it in details that, with experiment how the actual values experiment and theoretical prediction whether they match and if not then what are the reasons, what are the problems of the conversion types of negative electrode.

Then address the problem of negative electrode, that in general we will talk about. Then I will take a case study, again one material which is a spinel based material conversion type that was synthesized in our laboratory. And how they perform and whether we can understand this experimental results based on the theoretical knowledge that we have gained so far through other lectures. And finally, the electrochemical performance will be highlighted.

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Ideal properties of a Li ion anode Material

- An ideal anode must contain elements or compounds with low atomic or formula weights, low density and reversibly accommodate fairly large amounts of Li per formula unit to yield large, stable, and reversible gravimetric (mAh g^{-1}) and volumetric (mAh cm^{-3}) capacities.
- An ideal anode material must show a potential as close to that of Li metal as possible. This is because, when combined with a 4 V cathode, the overall working voltage of the LIB will not be much lower than 4 V.
- It must not be soluble in the electrolyte or chemically react with the salt or solvents of the electrolyte.
- It must possess good electronic and Li ionic conductivity ("mixed conduction") so that the electrode will have small impedance for current pick-up and for the motion of the Li ions within the active material.

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So, as you know that, an ideal anode must contain elements or compounds with low atomic or formula weights, low density and reversibly accommodate fairly large amount of lithium per formula unit to yield a large, stable and reversible gravimetric as well as volumetric capacities.

So, the idea is that, the weight of the alloy itself or the conversion material itself will be low; but it should accommodate large number of lithium, because obviously the to increase the N. Because you know that from the Faraday law, if I can increase the N and reduce the molecular mass; then suddenly I will gain the capacity. So, that is the only reason.

Second point which is important is that, the anode material must show a potential which is close to that of the lithium metal and that is due to the fact that, the voltage in window will be expanding if you do that. So, when you combined it with a 4 volt cathode, the working voltage for lithium ion battery will not be much lower than 4 Volt. But instead if

you take say LTO, which is having 1.5 volt plateau and work it with a 4 volt cathode, then you are losing voltage.

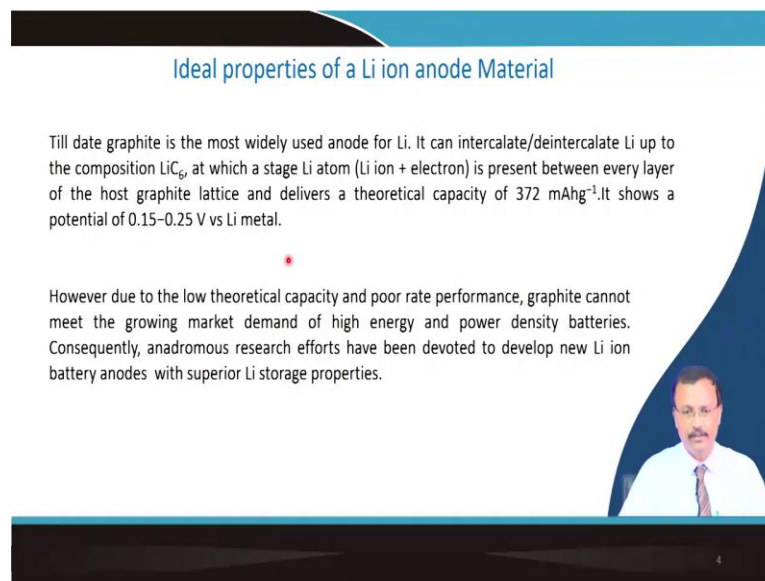
So, you will get roughly the capacity, the voltage roughly about 4 minus 1.5. So, 2.5 volt around you will get, also this is compositional dependent.

Third fourth, third category third criteria is, that it must not be soluble in the electrolyte or chemically react with salt or the solvent of the electrolyte; because of the obvious reason, if it forms a reaction product, it will get deposited, you will be losing the active mass and this may be impervious to the lithium ion movement.

So, it will be the losing the capacity. And finally, it must possess good electronic and lithium ion conductivity, because of the obvious reason; when something is getting oxidized, lithium will go into the electrolyte as a lithium plus ion, but the electron will flow out.

So, if your material itself is not electronically conducting, then electron cannot pass through the outer circuit. So, we need a mixed type of conductor. So, that it is having a small impedance for current pickup and for the motion of lithium ions within the active material. So, all this criteria this easily you can understand, you do not have to mug it up; but if you can know the actual feature of the requirements what you require, then suddenly this points will come to your mind.

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Ideal properties of a Li ion anode Material

Till date graphite is the most widely used anode for Li. It can intercalate/deintercalate Li up to the composition LiC_6 , at which a stage Li atom (Li ion + electron) is present between every layer of the host graphite lattice and delivers a theoretical capacity of 372 mAhg^{-1} . It shows a potential of 0.15–0.25 V vs Li metal.

However due to the low theoretical capacity and poor rate performance, graphite cannot meet the growing market demand of high energy and power density batteries. Consequently, anadromous research efforts have been devoted to develop new Li ion battery anodes with superior Li storage properties.

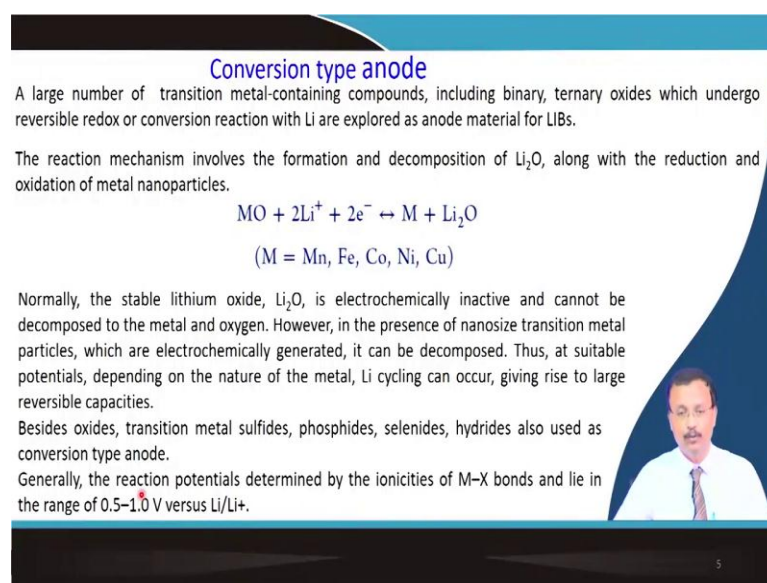
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So, graphite is the most widely used anode for lithium. So, it can intercalate and deintercalate lithium up to a composition of LiC_6 , that already you know [FL] at this stage lithium ion plus electron is present between every layer of the host graphite lattice. And you can calculate that it gives a theoretical capacity about 372 milli Ampere hour per gram and a potential which is ranging from 0.5 to 0.25 volt versus lithium metal, that already I have described in my earlier lectures.

Now, due to the low theoretical capacity and poor rate performance; rate performance means if you use this kind of battery for high rate application, if you drain lot of current, so graphite cannot meet the growing demand of the market for high energy and high power density batteries.

So, very rigorous research effort, research effort is being dedicated to develop new type of lithium battery anodes, which can store superior storage capacity as far as lithium is concerned.

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Conversion type anode

A large number of transition metal-containing compounds, including binary, ternary oxides which undergo reversible redox or conversion reaction with Li are explored as anode material for LIBs.

The reaction mechanism involves the formation and decomposition of Li_2O , along with the reduction and oxidation of metal nanoparticles.

$$\text{MO} + 2\text{Li}^+ + 2\text{e}^- \leftrightarrow \text{M} + \text{Li}_2\text{O}$$

(M = Mn, Fe, Co, Ni, Cu)

Normally, the stable lithium oxide, Li_2O , is electrochemically inactive and cannot be decomposed to the metal and oxygen. However, in the presence of nanosize transition metal particles, which are electrochemically generated, it can be decomposed. Thus, at suitable potentials, depending on the nature of the metal, Li cycling can occur, giving rise to large reversible capacities.

Besides oxides, transition metal sulfides, phosphides, selenides, hydrides also used as conversion type anode.

Generally, the reaction potentials determined by the ionicities of M-X bonds and lie in the range of 0.5–1.0 V versus Li/Li+.

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So, large number of transition metal containing compounds, that includes binary compound or ternary compounds; that actually undergoes reversible redox conversion type of reaction with lithium. So, they are explored as anode material for lithium ion battery.

So, I already described it, but let us have a re look at it, the reaction mechanism that involves the formation and decomposition of lithium oxide along with the reduction and oxidation of metal nano particle. So, you take an oxide, then lithium is coming, then it gets reduced this oxide get reduced to form metal particle, which is having zero charge and Li_2O is form.

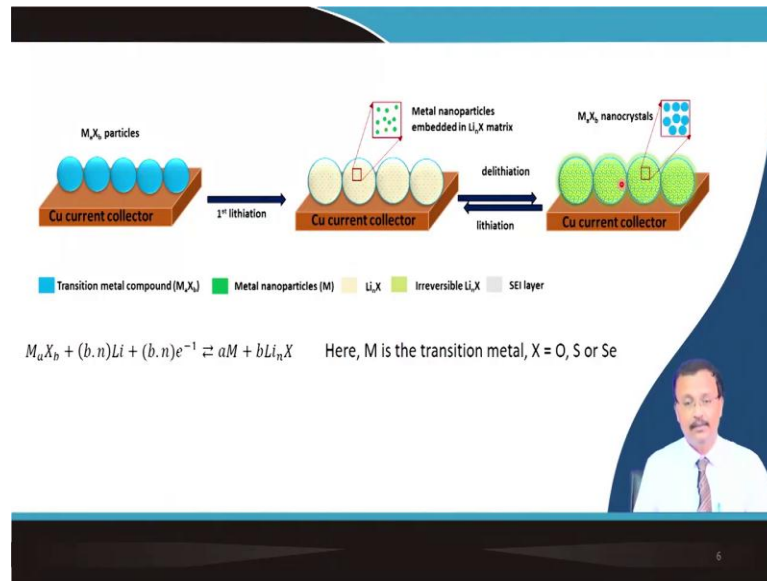
So, in fact in the matrix of Li_2O , you have metal particles. So, this is one of the mechanisms, one of the step one of the mechanism for conversion type of cathode. This MO or this MO is basically based on transition metal oxide, which has been told here. So, it is manganese, iron, cobalt, nickel, copper they are used. Normally, the stable lithium oxide, this lithium oxide is electrochemically inactive and that cannot be decomposed to metal and oxygen.

But when this nanosize transition metal particles, which are electrochemically generated like this, it can be decomposed. So, it is possible to decompose this. Thus, at suitable potential, depending on the nature of this metal, lithium cycling can occur giving rise to a large reversible capacity.

So, what is happening here, this metal and lithium they start to form an alloy and then lithium cycles within that alloy and then you get a reversible type reaction going on cycle after cycle and that is the basis of this type of conversion type anode. Not only oxide; you can use metal sulfides, phosphides, selenides, hydrides they also can have similar kind of behavior.

So, most of these materials are yet unexplored. So, lot of scope to do research to find a good quality anode material. The reaction potential determined by the ionicity of this metal and X bond and lie in the range of 0.5 to 1 volt versus lithium. So, if you are using this, then during alloying, the voltage range is indeed of our use, whatever we are looking for a lower anode potential to maximize the voltage window of the full cell.

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So, this is one example that how exactly it happens. So, you know in the current collector, you have this kind of particle, it could be oxide also. So, this is a transition metal compound M_aX_b ; during 1st lithiation, you can see metal nanoparticle they are embedded in lithium oxide or X's a some other material other than oxide, so it is embedded there.

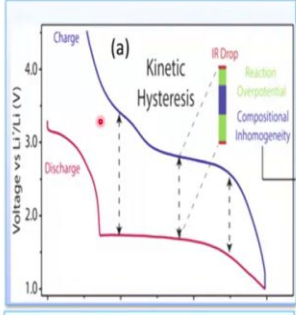
And then it starts to form upon lithiation and delithiation; it can have this kind of nanocrystal, so that is there. So, the reaction scheme is exactly follow something similar to whatever we just explained.

Now, one thing is that, that the formation of SEI layer; because the electrode is dipped into the electrolyte, that is almost unavoidable to form. So, the characteristics of SEI must be properly manipulated.

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Problems associated with conversion materials

Voltage Hysteresis: A major factor that hinders the practical application of conversion anodes is the low round-trip energy efficiency due to the voltage hysteresis between the charging and discharging profiles, i.e., charging occurs at a higher voltage compared to discharging, indicating that the amount of energy retrieved back is less than the energy stored in each cycle.

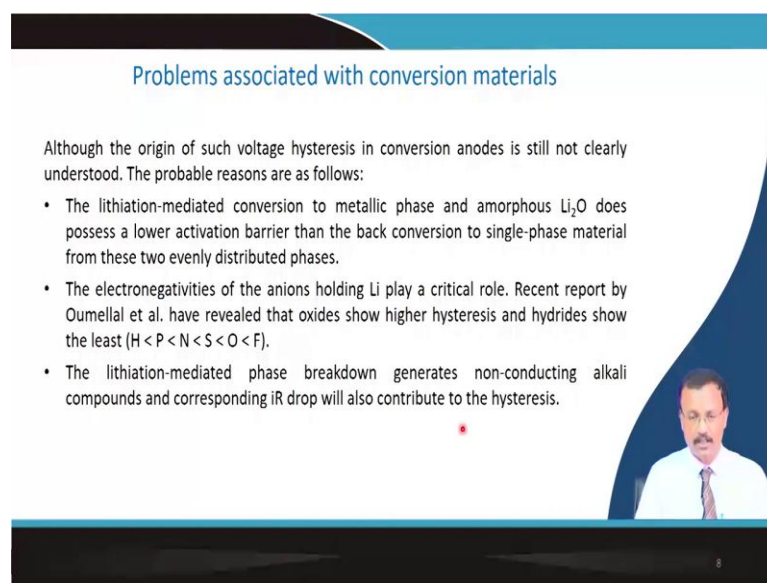


The graph (a) plots Voltage vs Li⁺/Li (V) on the y-axis (ranging from 1.0 to 4.0) against an unlabeled x-axis. It shows two curves: a blue 'Charge' curve and a red 'Discharge' curve. The charge curve starts at approximately 3.5V and drops to about 1.5V. The discharge curve starts at approximately 1.5V and rises to about 3.5V. The area between the two curves is labeled 'Kinetic Hysteresis'. A legend on the right identifies three components: 'IR Drop' (red), 'Reaction Overpotential' (green), and 'Compositional Inhomogeneity' (blue). A small inset image of a man in a white shirt and tie is visible in the bottom right corner of the slide.

Major problem that hinders the practical application of this conversion anode is the low round trip energy efficiency due to the voltage hysteresis, that you can see between the charging and discharge. So, if this is your charge part and this is your discharge part. So, you can see that there is a large hysteresis; ideally the voltage difference should not be there.

But this voltage hysteresis between the charging and discharging profile to be more precise during charging, it occurs at higher voltage as compared to discharging and that eventually indicates that the amount of energy that is retrieved back is less than the energy stored cycle. So, that problem is there.

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Problems associated with conversion materials

Although the origin of such voltage hysteresis in conversion anodes is still not clearly understood. The probable reasons are as follows:

- The lithiation-mediated conversion to metallic phase and amorphous Li_2O does possess a lower activation barrier than the back conversion to single-phase material from these two evenly distributed phases.
- The electronegativities of the anions holding Li play a critical role. Recent report by Oumellal et al. have revealed that oxides show higher hysteresis and hydrides show the least ($\text{H} < \text{P} < \text{N} < \text{S} < \text{O} < \text{F}$).
- The lithiation-mediated phase breakdown generates non-conducting alkali compounds and corresponding IR drop will also contribute to the hysteresis.

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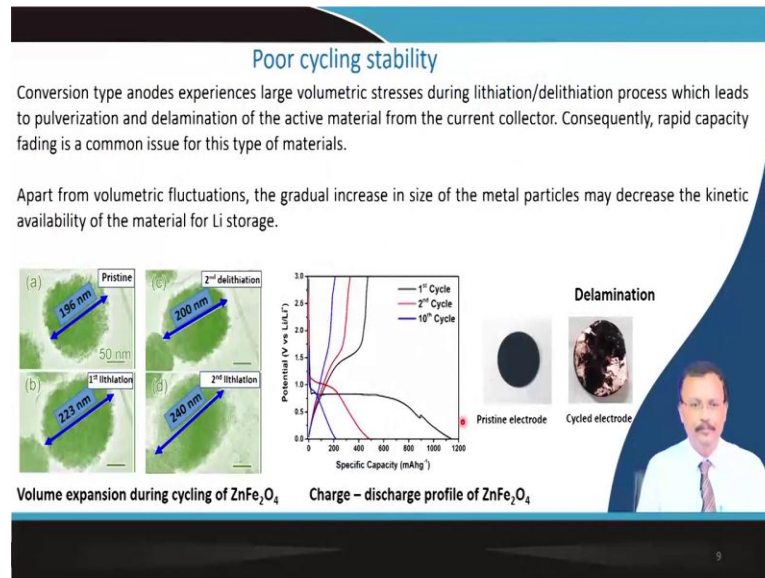
So, the origin of such voltage hysteresis in conventional anode is not really clearly understood. So, we can only cite couple of reasons. So, one of the reasons that is the lithiated or the lithiation mediated conversion to metallic phase and amorphous type of lithium oxide does possess a lower activation barrier; then the back conversion of a single phase material from these two evenly distributed phases. So, that can cause the hysteresis part.

Second factor is the electronegativity of the anions that holding the lithium, that actually play a very major role. So, in one of the recent report by this fellow Oumellal; they have revealed that the oxide in fact, show this higher kind of hysteresis and hydride they show the lowest. So, it goes like this.

So, best is fluoride extremely dangerous to work on; an oxide is here, but hydride is here. So, that tells us that we should also explore not the oxides, but other type of transition metal hydride or phosphite or nitrite for this purpose. Finally, the lithiation mediated phase diagram generates a non conducting alkali compound and corresponding IR drop will also contribute to the hysteresis.

So, you know the IR drop, the due to the resistance increase that basically can change this voltage, the difference can be expanded during voltage hysteresis as I have just shown.

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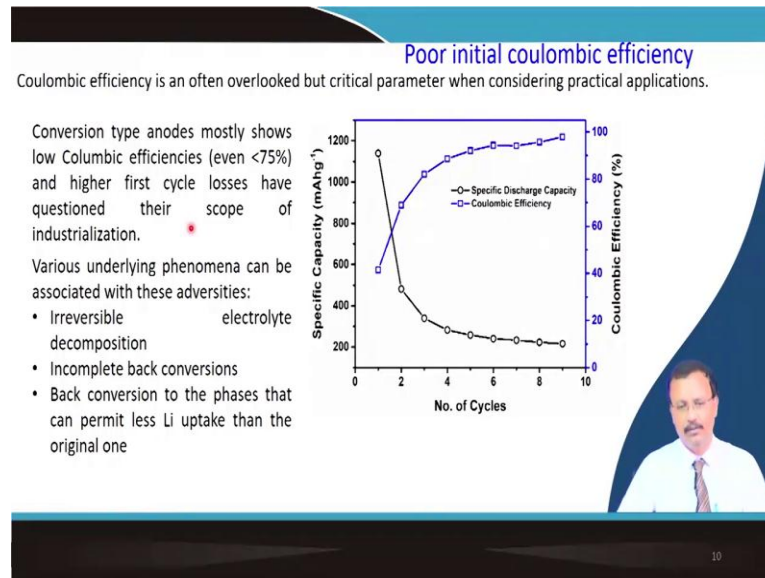
Now, usually conversion type anodes, they also expand experience a large volume stress, mainly due to lithiation and delithiation process, which leads to pulverization and delamination of the active material, the same way that we showed earlier. So, that leads to rapid capacity fading and this is a common issue for this type of material, irrespective of the type of the transition metal oxide, you cannot avoid it.

Apart from volumetric fluctuation, the gradual increase of the size of the metal particle that may also decrease the kinetics, kinetic availability of the material for lithium storage. So, actually the diffusion distance increases as the volume increase. And this is one of the examples that the consequences of this as you can see, the charge discharge profile of the material of our interest zinc ferrite, we took the photograph here.

So, as you can see pristine material is 196, second delithiation is 200, then 223, and then finally, 240. And it is affecting the discharge capacity, the voltage is increasing here; there is a large hysteresis whatever we showed and progressively with number of cycles you can see that, you have progressive increase in the voltage.

And finally, the outcome of this is the delamination. So, you have the electrode initially like this and then once you cycle it maybe 200, 300 cycles; then it delaminates and then it goes into the electrolyte. So, you have no more perfect coating on the current collector, which is copper in this case.

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So, the coulombic efficiency is often overlooked, but critical parameter; this is one of the critical parameter when consider a practical application. So, as I said the conversion type anodes mostly shows lower coulombic efficiency, you can see as low as 75 percent and higher first cycle losses.

In the last view graph you have seen that, if you see the first discharge curve, it is dramatically fall after second cycle here. So, this is the problem. So, if I consider for commercialization, these are the two question that we will have to understand and we will have to delimitate this, delineate this difficulties.

So, various factor can be responsible for this; one could be irreversible electrolyte decomposition and of course, electrolyte decomposition will be irreversible, because it cannot form back the original electrolyte. In complete back conversion that is also another reason and back conversion to the phases that can permit less uptake of lithium from their original one.

So, this is something related to the SEI formation; if it is impervious to lithium, then certainly you will be losing lithium. So, your charge capacity will be higher, discharge capacity will be higher than the charge capacity. Remember for this material, since they do not have any lithium, always you will have to lithiate it; so that means you will have to discharge fast and then subsequently you can charge and take back this lithium.

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Poor initial coulombic efficiency

Most of the literatures report the half- cell performance of the conversion type anode where plenty of Li is available as Li metal foil is used as anode. However, when a full Li-ion cell is assembled, as the Li ions are hosted in cathode, the available Li is limited. Therefore, if large amount of Li is irreversibly lost in anode side, the total full cell capacity will decrease.

Commercial graphite anodes with a specific surface area of a few $\text{m}^2 \text{g}^{-1}$ or less exhibit good first cycle CE on the order of 90–95% (first cycle irreversible losses of 5–10%).

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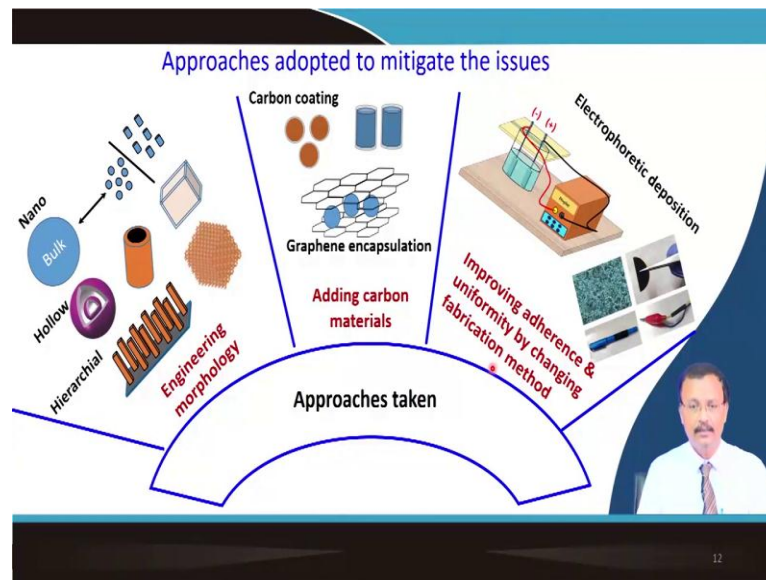
So, most of the literature report half cell performance of the conversion type anode where plenty of lithium is available in the lithium metal foil are used as anode. So, this is the thing that I was mentioning. So, as such this conversion material they do not have any lithium in it and you are measuring it with lithium metal.

So, in half cell configuration. So, no matter if lithium is lost, you have enormous source of lithium for the discharged reaction to take place; unless there is an SEI layer form, which is impervious for the lithium to enter and form the alloy. But when you are considering a full cell, then you are limited by your lithium amount. So, when a full cell lithium, lithium ion cell is assembled.

So, as the lithium ions are hosted in the cathode, the available lithium is limited; therefore if large amount of lithium is irreversibly lost in the anode size, the total full capacity will decrease. So, commercial graphite anode with a specific surface area with few meter square per gram or less exhibit, good first cycle cyclic ability or columbic efficiency about 90 to 95 percent; first cycle irreversible losses are only 5 to 10 percent.

So, when you compare graphite with the conversion type anode, always you have something in mind why should I go for it; because of this problem, the hysteresis, voltage hysteresis, low columbic efficiency, enormous discharge versus charge, so that columbic efficiency is quite high and then volume expansion, then delamination, pulverization. So, these problems are there.

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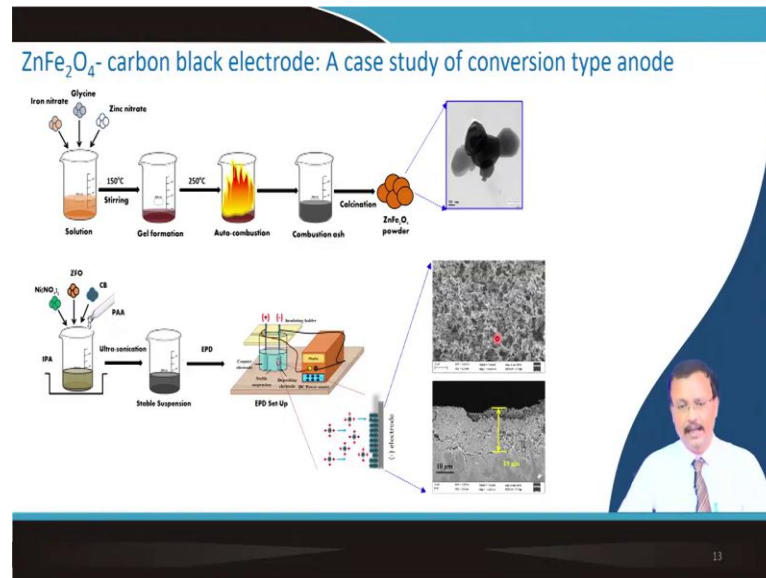


So, there are various approaches that is adopted to mitigate this issue. The first one is different types of engineered morphology that one can do; nano sizing is one of them, then hollow structure like this or like this, this is another thing or the structure for silicon anode, I described the brush bristle like structure, the structure of your toothbrush.

So, this kind of structure is also beneficial to circumvent these problems. Second one is carbon coating. So, idea is that this carbon material which encapsulate this types of alloy material what they will act as a buffer and mitigate the stress effect. The third one which we thought that this will be beneficial is to actually enhance the adhesion between the electrode material and the active material. So, this adhesion is most cases if you do tape casting, this is poor, so that the delamination is expedite.

So, if you can devise a certain deposition like electrophoretic deposition, where charged particles are forced onto the substrate for a uniform deposition. So, that could be a solution to make a very strong bond between the active material and the current collector. So, that the delamination even if it volume expansion takes place, pulverization takes place, so that is not basically detrimental. So, that was thought of.

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So, one can prepare this zinc ferrite, which is not very good electronic conductor spinel based material with a carbon black some kind of composite by a auto combustion process. So, this has been shown; we have taken iron nitrate, glycine and zinc nitrate. So, these are the fuel and reducer.

And then it forms a gel and then it catches fire and then you get a combustion ash; once you calcine it, then you get this zinc ferrite powder. And you take the TEM exactly you see that the size is about 200 nanometer and due to this it is quite agglomerated.

Then you take this powder along with nickel nitrate, which is a charger to control their surface charge properties; then conducting black and a binder in terms of PAA and you mix it here and form some kind of stable suspension. And this stable suspension you take in a EPD setup, electrophoretic deposition setup. So, already you have it charged positively, because of the addition of nickel nitrate inside the suspension.

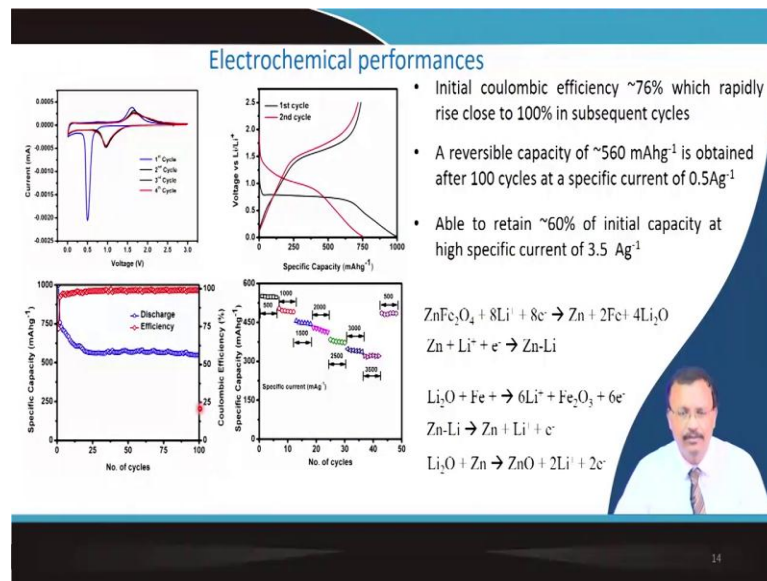
And apply a DC voltage and keep your electrode material connected with negative terminal of the battery at a small DC power source. And then these charged particles, they will be attracted and very uniform coating that you will see; it is not only uniform, but it is porous as well.

So, you can see the microstructure it is quite porous and you can see the cross section of this kind of deposition typically about 19, 20 micron that you can deposit here. You can

control this thickness by controlling the voltage and deposition time and you get a very stable porous layer by this electrophoretic deposition technique. This is not very well explored in the literature or in the book you will not find it, electrophoretic deposition is a very well known practice.

But the use of electrophoretic deposition in the battery research, that is not very well explored.

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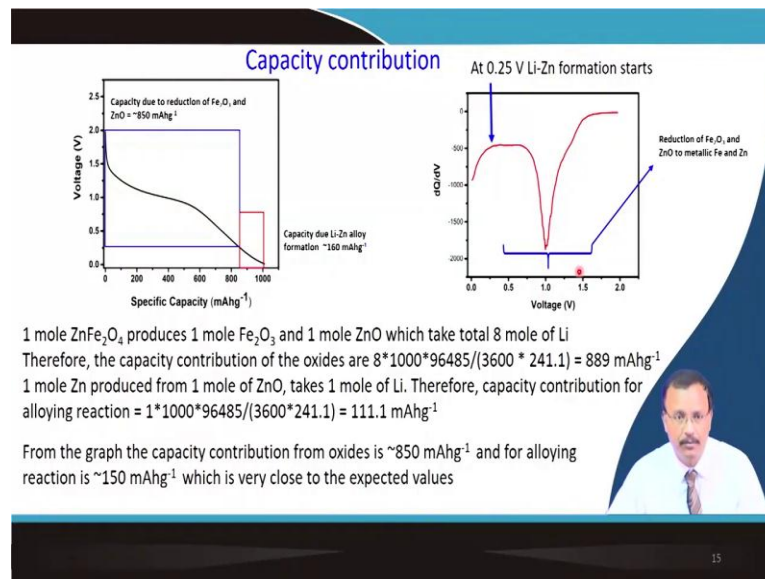
So, now, you can in the half cell configuration, you can study the electrochemical performance and you can see the charge discharge and cyclic voltammetry, all this kind of thing you can measure or the cyclability or the rate performance this you can measure, the way we have measured for other types of electrode material.

So, initial columbic efficiency is 76 percent that cannot be avoided and rapidly it rises close to 100 percent. So, initial problem will be there; because your this oxide material is transformed into lithium L i 2 O and with the metallic particle. So, there will be some kind of, some kind of fast discharge capacity will be higher, this is almost unavoidable.

But a more or less good reversible capacity you can achieve about 560 which is not that bad; even after 100 cycles, when we discharge it at 0.5 Ampere per gram, this rate. So, it can as you can see, it can have about 60 percent of its initial capacity when you increase the current, the drain drained current, the discharge current is 3.5 Ampere per gram.

So, these are the actual this thing reaction that I was talking about; you see since this is not a mono oxide like titanium oxide or manganese oxide, zinc and iron both metallic form forms in L i 2 O matrix. And then eventually the zinc forms an alloy and followed by lithium again reacts with this and then it forms iron oxide and zinc also reacts with lithium to form this and L i 2 O reacts with zinc to form zinc oxide. So, it is a reversible type that keeps on going, once you repeat the charge and discharge cycle.

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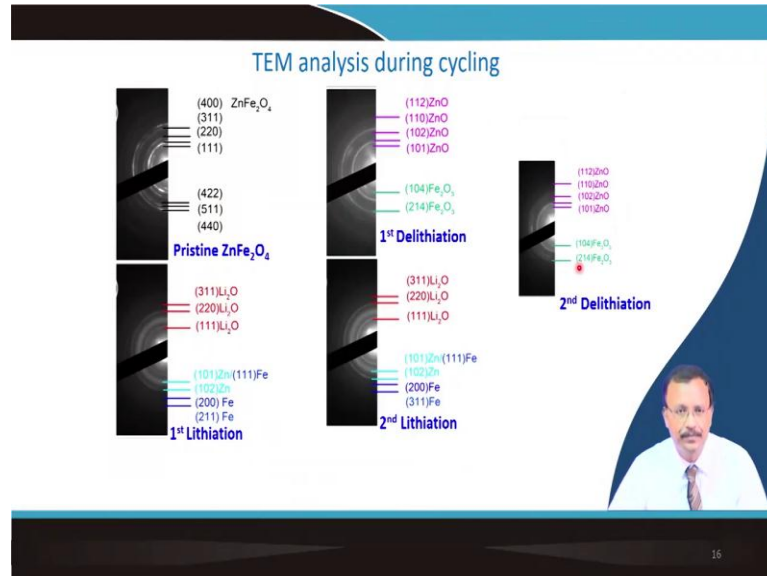
So, the capacity contribution you can estimate, in fact I was thinking to ask you to calculate that. So, as you can see 1 mole of zinc ferrite that produces 1 mole of iron oxide and 1 mole of zinc oxide. So, that takes total 8 mole of lithium.

So, the capacity contribution of the oxide, you can calculate 8 into 1000 into Faraday constant 3600, that is just a time conversion factor into 241.1. So, it is coming about 889 milli Ampere hour per gram. Then 1 mole of zinc produced from 1 mole of zinc oxide that can take 1 mole of lithium, so the capacity contribution is 111. From the graph, the capacity contribution of oxide is 850 and for alloying it is 150, which is very close to the expected value.

So, this is basically supporting the kind of the kind of reaction mechanism that we can think of and simultaneously we can estimate that what exactly in this plateau considering this plateau, whether this capacity actually matches with the thing. And differential

capacity analysis that is also another way to understand the exact voltage, where this reaction takes place. So, this is another example of the differential capacity plots.

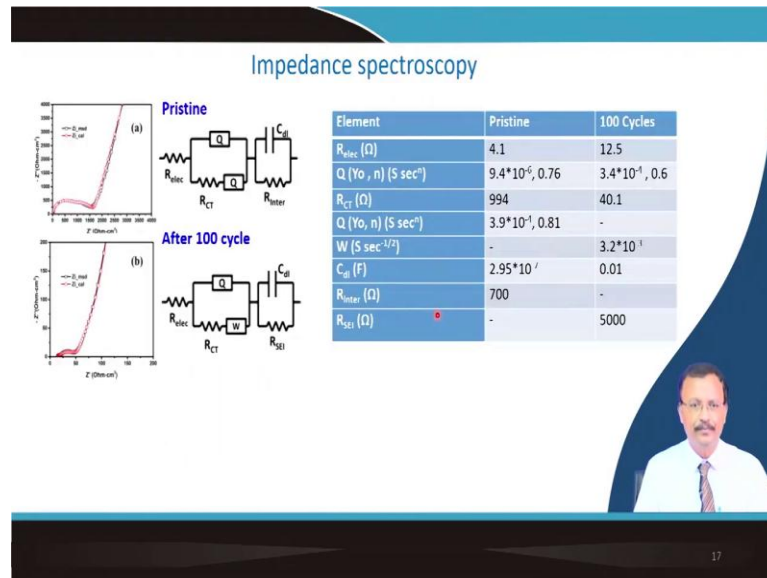
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Then one can do the TEM analysis to exactly know the reaction mechanism. So, as you can see at different stage like pristine, zinc ferrite, then first lithiation, then second first delithiation, second lithiation, again second delithiation; we have analyzed this TEM pattern to see that indeed that these are the material whatever theoretically we were suspecting that they form.

Instead of doing XRD, we have done the TEM analysis this time to know the exact phase which ever has formed.

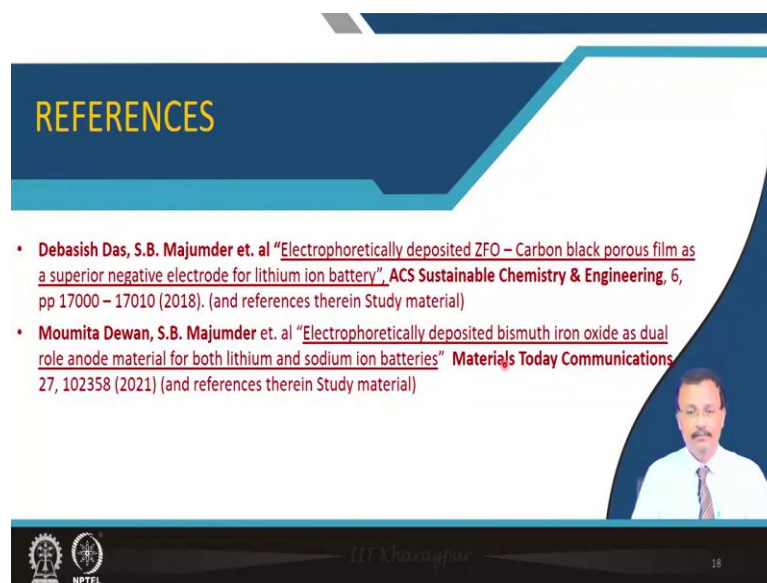
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So, after that we undertook the impedance spectroscopy analysis and here also the randle circuit is more or less in line, whatever I already described in my earlier lecture. So, wanted to know that in pristine and after 100 cycles, what are exactly the things that is changing. So, here you can see the electrolytic resistance that is increased, right. Then you can see the other SEI formation after 1000 cycles; the pristine it will not be there, but after 1000 cycles it is too much.

So, although the reactions are quite complicated, but as I said this kind of analysis can give you sufficient information, that what exactly is going on in the material itself.

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REFERENCES

- Debasish Das, S.B. Majumder et. al "Electrophoretically deposited ZFO – Carbon black porous film as a superior negative electrode for lithium ion battery", *ACS Sustainable Chemistry & Engineering*, 6, pp 17000 – 17010 (2018). (and references therein Study material)
- Moumita Dewan, S.B. Majumder et. al "Electrophoretically deposited bismuth iron oxide as dual role anode material for both lithium and sodium ion batteries" *Materials Today Communications* 27, 102358 (2021) (and references therein Study material)

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So, this is the typical reference the study material that you are supposed to follow; this is two of our papers, which basically talk about this zinc ferrite whatever I have presented. And there is this is another recent paper, where a completely different material that is also oxide; where bismuth iron oxide it is a multifunctional material, it is having a good magnetic property, good ferroelectric property and along with that photocatalytic activity is also there.

So, we just wanted to see that if that also can be used as the anode material. So, this part also we will find it interesting and all the reaction mechanisms, capacity calculations and other readymade details that will be useful for you to study.

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CONCLUSION

- Conversion type negative electrodes: Associate problems
- Approaches to overcome the associate problems
- Spinel zinc ferrite as negative electrode material for Li ion rechargeable cell
- Cyclic voltammetry, charge – discharge, cycleability, and rate performance
- TEM and EIS analyses

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So, conversion type negative electrodes, their associated problem we have talked about. The approach to overcome the associated problem that has been highlighted and for that we have introduced electrophoretic deposition to get a well adhered film on the substrate. Then spinel zinc ferrite as negative electrode material we have introduced for lithium ion rechargeable cell.

So, it is not very well established yet, it is not a textbook kind of stuff; but just I wanted to show that experimentally how things actually behave and whether it is in line to the theoretical knowledge, that you are gaining through this course.

Then cyclic voltammetry, charge discharge, cycleability and rate performance, this characteristics in half cell configuration we have introduced. And finally, TEM and e EIS analysis; TEM was done to understand that indeed this phases has formed and EIS analysis was done to understand that what exactly is happening after cycling, so that it deteriorates the property of this kind of anode material.

Thank you for your attention.