Electrochemical Energy Storage
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Module - 03
Lithium batteries
Lecture - 11
History and Categories of Lithium Batteries

Welcome to my course Electrochemical Energy Storage, and this is module number 3 where we will talk exclusively on Lithium Batteries. And, this is lecture number 11 where I will introduce the History and different categories of Lithium ion batteries.

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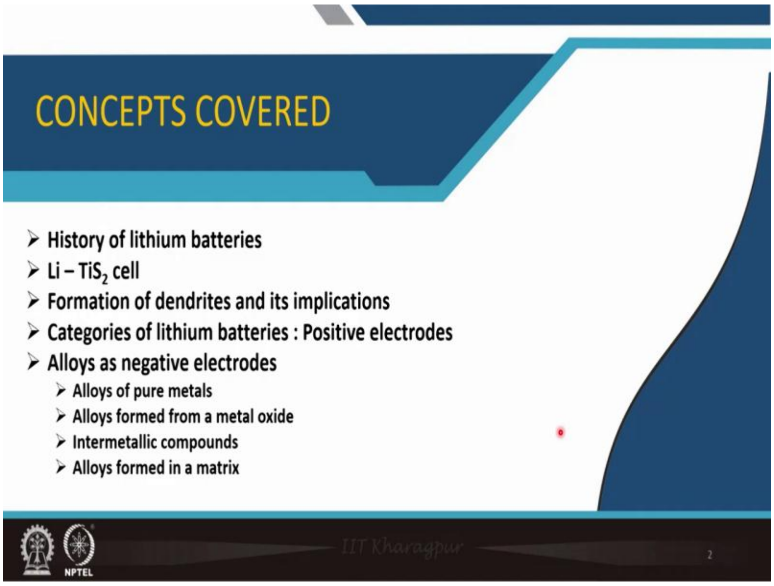

CONCEPTS COVERED

- History of lithium batteries
- Li – TiS_2 cell
- Formation of dendrites and its implications
- Categories of lithium batteries : Positive electrodes
- Alloys as negative electrodes
  - Alloys of pure metals
  - Alloys formed from a metal oxide
  - Intermetallic compounds
  - Alloys formed in a matrix

So, first we will talk about the history of lithium ion battery, where from it started. Then I will show you the image of the first lithium ion cell which had lithium as one of the metal anode and titanium disulfide as cathode material. While I was talking about the crystal structure, already I introduced molybdenum disulfide. So, titanium disulfide was used as one of the positive electrode materials.

Then the implication of using lithium metal as negative electrode, that will be described in terms of the formation of the dendritic growths, and what are the implications of this dendrite growth. Then we will talk about various types of lithium ion batteries, what are the positive electrodes that is used there and then what are the negative electrodes.

So, apart from this carbonaceous graphite or MCMB there are other materials also people are working on which is alloy of pure metals or in some case semiconducting silicon or other metals that is also used in form of metal alloys. Then alloy that is formed from a metal oxide, so, that will also be introduced. Intermetallic compounds and alloy formed in a matrix. So, these are some of the important material that we will talk about in this lecture.

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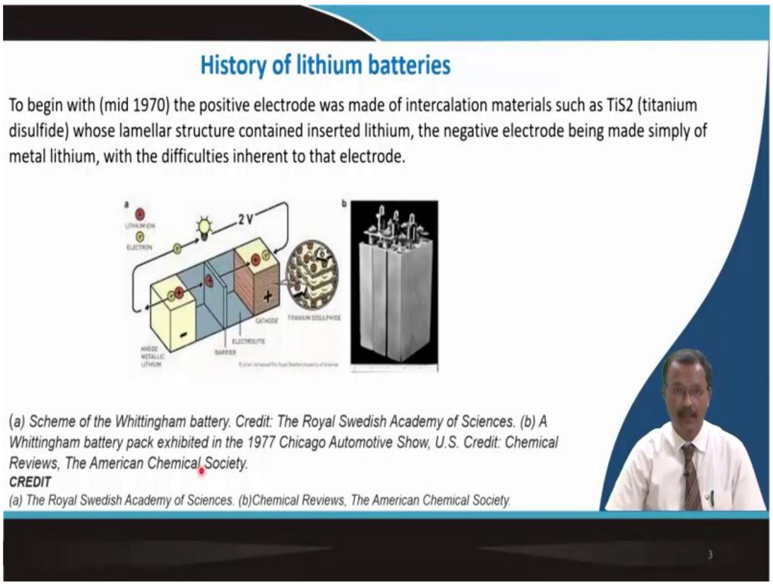

History of lithium batteries

To begin with (mid 1970) the positive electrode was made of intercalation materials such as TiS2 (titanium disulfide) whose lamellar structure contained inserted lithium, the negative electrode being made simply of metal lithium, with the difficulties inherent to that electrode.

(a) Scheme of the Whittingham battery. Credit: The Royal Swedish Academy of Sciences. (b) A Whittingham battery pack exhibited in the 1977 Chicago Automotive Show, U.S. Credit: Chemical Reviews, The American Chemical Society.

CREDIT

(a) The Royal Swedish Academy of Sciences. (b)Chemical Reviews, The American Chemical Society.

So, it all begin in mid 70’s, the positive electrode was made out of intercalation material like titanium disulfide. As you can see it is having a lamellar structure, and this lamellar structure contained inserted lithium and as a negative electrode being made simply the use of metallic lithium. So, this is anodic metallic lithium, but certain difficulties are inherent to this metallic lithium.

So, if you look at the voltage; that is basically the difference in chemical potential of lithium in lithium metal and in the positive electrode that will actually lead a 2 volt battery. So, in terms of energy density it is not that good, because amount of charge store and the voltage that it is generating that gives the energy and 2 volt is low in that respect.

And, this is the cell that constitutes several of this type of anode and cathode. Each individual cell they are connected in series so that you can increase the voltage and if you join it in parallel then you can increase the capacity.

So, we call this is a Whittingham battery, and I have taken it from the Royal Swedish Academy of Science the figure; I acknowledge the incorporation of the figure. And this is the battery pack which was developed in 1977 and it was displayed in Chicago Automotive Show and this is also acknowledged. So, this is one of the first lithium ion battery using lithium metal as negative electrode material.

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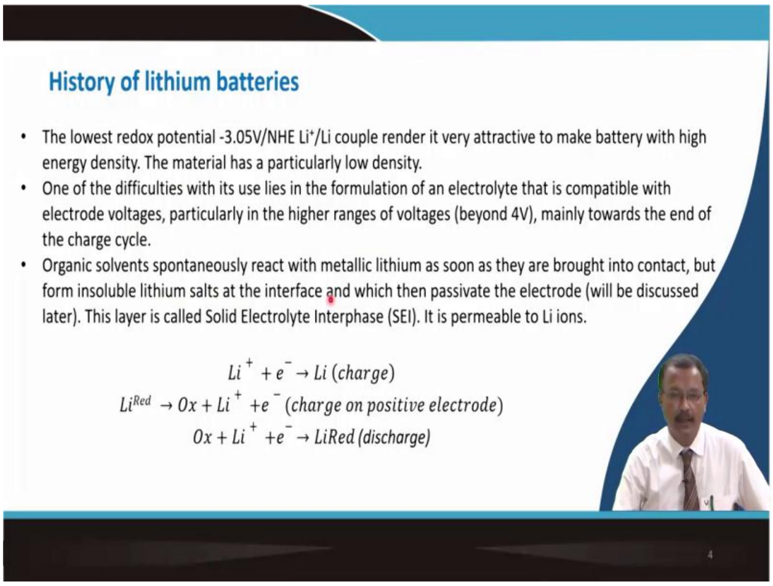

History of lithium batteries

- The lowest redox potential -3.05V/NHE Li^+/Li couple render it very attractive to make battery with high energy density. The material has a particularly low density.
- One of the difficulties with its use lies in the formulation of an electrolyte that is compatible with electrode voltages, particularly in the higher ranges of voltages (beyond 4V), mainly towards the end of the charge cycle.
- Organic solvents spontaneously react with metallic lithium as soon as they are brought into contact, but form insoluble lithium salts at the interface and which then passivate the electrode (will be discussed later). This layer is called Solid Electrolyte Interphase (SEI). It is permeable to Li ions.

$$Li^+ + e^- \rightarrow Li\ (charge)$$
$$Li^{Red} \rightarrow Ox + Li^+ + e^-\ (charge\ on\ positive\ electrode)$$
$$Ox + Li^+ + e^- \rightarrow LiRed\ (discharge)$$

Now, the lowest redox potential of this redox couple oxidized state is lithium plus and lithium metal is it is in reduced form. And if you measure the voltage the way I introduced in the first lecture or the basic electrochemistry with respect to hydrogen electrode, you will get a negative potential negative reduction potential of minus 3.05 volt. And it is very attractive to make the battery with high energy density.

So, the material as I explained that it is basically having a relatively lower energy density because of the voltage that you are getting. So, one of the major difficulties with this type of battery that lies in the formation of a of an electrolyte solid state that is compatible with electrode voltage. Particularly in higher range of voltage beyond 4 volt mainly towards the end of the charge circle cycle, whenever you get 4 volt around. So, we will find that this kind of layer solid electrolyte layer that forms.

And this is due to the reason that the organic solvent that we are using that spontaneously react with the metallic lithium almost instantaneously when you bring lithium in contact with the electrolyte. But eventually it forms insoluble lithium salts at the interface and then it passivates the electrode. So, we will discuss this more in the latter part of the lecture.

And, this kind of layer that is formed we call it is a solid electrolyte interface which is abbreviated as SEI, but it permeates lithium ions it allows lithium ions to flow. So, if you just see the reaction mechanism, the lithium is getting oxidized forming lithium ion, an electron that passes through the external circuit.

So, it forms on positive electrode, you have the positive electrode in the form of your titanium disulfide and lithium is intercalated and it is getting reduced to form lithium. So, this is charge on the positive electrode. And, eventually during discharge, what happens that from the positive electrode lithium goes out and it takes electron from the external circuit and it gets reduced during discharge; a very simplified reaction mechanism that you can think of.

$$Li^{+}\overset{+}{} + e^{-}\overset{-}{} \rightarrow Li\ (charge)$$

$$Li^{Red} \rightarrow Ox + Li^{+}\overset{+}{} + e^{-}\overset{-}{} \quad (charge\ on\ positive\ electrode)$$

$$Ox + Li^{+} + e^{-} \rightarrow Li^{Red}\ (discharge)$$

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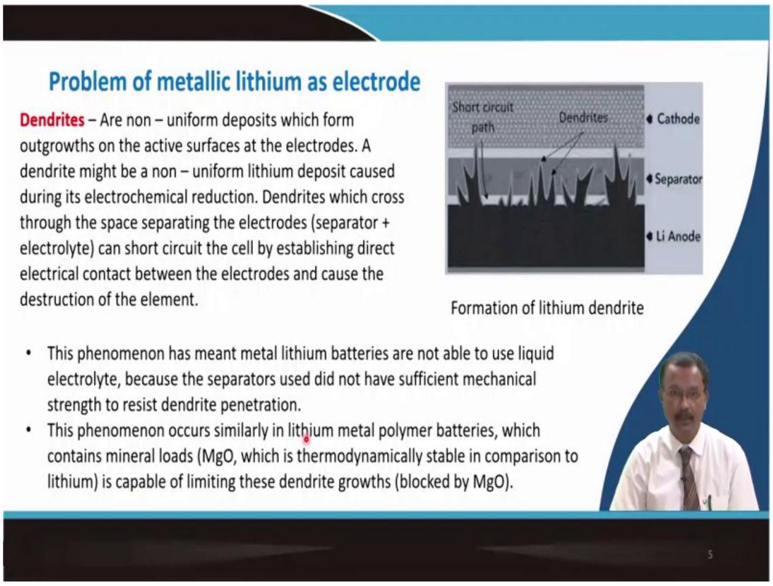

Problem of metallic lithium as electrode

Dendrites – Are non – uniform deposits which form outgrowths on the active surfaces at the electrodes. A dendrite might be a non – uniform lithium deposit caused during its electrochemical reduction. Dendrites which cross through the space separating the electrodes (separator + electrolyte) can short circuit the cell by establishing direct electrical contact between the electrodes and cause the destruction of the element.

Formation of lithium dendrite

- This phenomenon has meant metal lithium batteries are not able to use liquid electrolyte, because the separators used did not have sufficient mechanical strength to resist dendrite penetration.
- This phenomenon occurs similarly in lithium metal polymer batteries, which contains mineral loads (MgO, which is thermodynamically stable in comparison to lithium) is capable of limiting these dendrite growths (blocked by MgO).

So, basically here lithium which is coming back from the positive electrode you can see that this lithium is electroplated on the surface of lithium metal, and this is not a uniform deposition. So, when it deposits; why when it will deposit? When it is charged the battery is charged. So, from the positive electrode lithium will come out and flow through the electrolyte and eventually it deposits on the metallic lithium.

So, these are non-uniform deposits and which forms some kind of outgrowth as you can see here. So, this is some kind of outgrowth and it basically tries to puncture the separator which is soaked with electrolyte. And these are when it basically touches the cathode, so it forms a short circuit path.

So, this dendrite growth is detrimental. So, this dendrite might be a non-uniform lithium deposit and this is caused during the electrochemical reduction. And dendrites will cross through the space separating the electrode that is separator and electrolyte.

And, as I told it can short circuit the cell by establishing the direct electrical contact between the electrodes and that cause the destruction of the element. So, metallic lithium although it offers you a higher potential window and thereby increase the energy density of the cell, this is not practically used for any commercial cell.

So, metal lithium batteries they are not in use with liquid electrolyte, because as I told the separator used did not have sufficient mechanical strength. We will talk about the separator in my forth coming lectures; that what kind of separator that is required which are strengthened enough.

There are various mechanism adopted to strengthen this kind of separators and they can resist dendritic penetration, so puncture strength should be high. But usually the normal commercially available separator they do not have sufficient mechanical strength.

And, this phenomenon similarly occurs in lithium metal polymer battery. So, polymer battery still uses lithium metal and which contains some kind of mineral loads like magnesium oxide which is thermodynamically stable in comparison to pure lithium. And that is basically capable of limiting this kind of dendrite growths. So, this is basically blocked by magnesium oxide.

So, that is one way this negative effect has been overcome by the formation of the dendrite has overcome by putting mineral loads like magnesium oxide.

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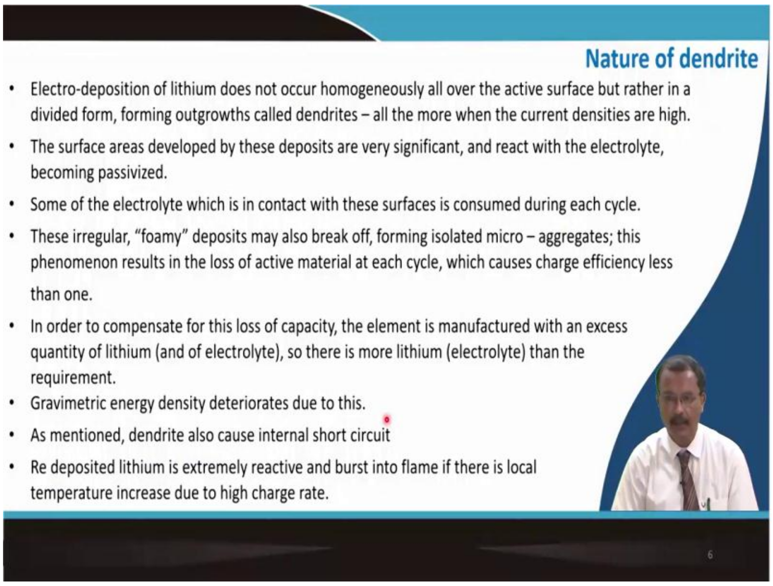

Nature of dendrite

- Electro-deposition of lithium does not occur homogeneously all over the active surface but rather in a divided form, forming outgrowths called dendrites – all the more when the current densities are high.
- The surface areas developed by these deposits are very significant, and react with the electrolyte, becoming passivized.
- Some of the electrolyte which is in contact with these surfaces is consumed during each cycle.
- These irregular, "foamy" deposits may also break off, forming isolated micro – aggregates; this phenomenon results in the loss of active material at each cycle, which causes charge efficiency less than one.
- In order to compensate for this loss of capacity, the element is manufactured with an excess quantity of lithium (and of electrolyte), so there is more lithium (electrolyte) than the requirement.
- Gravimetric energy density deteriorates due to this.
- As mentioned, dendrite also cause internal short circuit
- Re deposited lithium is extremely reactive and burst into flame if there is local temperature increase due to high charge rate.

So, let us have a look of the nature of the dendrite. So, this is basically electro deposition of lithium that does not occur; as I said homogeneously all over the active surface, but rather in a divided form forming outgrowth which is called dendrite. And this is more dendrite formation is more when the current density is high.

So, if you are discharging the battery at higher current rate then this, or charging the battery at higher current rate then this kind of formation is more. So, the surface areas developed by these deposits are very significant that react with a electrolyte and becomes passivated. So, electrolyte also in the charge state particularly they react with the electrolyte and forms some kind of passivation layer.

Some of the electrolyte which is in contact with these surfaces is consumed during each cycle. So, when the electrolyte is getting dissociated; so in the process the concentration of the electrolyte which is usually one mole of LiPF6 dissolved in EC DMC 1 is to 1 volume ratio. So, that is getting consumed.

The nature of this irregular deposits are foamy type and therefore, it breaks up. So, it forms isolated micro aggregates. And this phenomena actually results the loss of material at each cycle, because it forms a loose aggregate. So, you are losing lithium. So, charge deficiency is less than 1; the coulombic efficiency for this type of process is always less than; 100 percent coulombic efficiency is difficult to get.

So, in order to compensate this loss of capacity the element is manufactured with excess quantity of lithium. So, you put more lithium particularly in the electrolyte instead of 1 molar solution you increase it. So, more lithium in the electrolyte than the requirement and that basically reduces the gravimetric energy density, because you are using you are increasing the weight. So, your gravimetric energy density will be compromised. So, that is the next point.

And, also I mentioned that this dendrite that can cause the internal short circuit. And redeposited lithium is extremely reactive and since they are very reactive whichever is in this foamy deposit which are getting deposited on the lithium surface; say sometimes there are internal short circuit and burst into film flame. So, it catches fire because your organic electrolyte are flammable.

So, particularly at high charge rate the deposition is discrete, it is foamy in nature, forms dendrite, forms internal short circuit and then it burst into flame and catches the electrolyte catches fire. So, that all are very very detrimental for the performance of this kind of battery.

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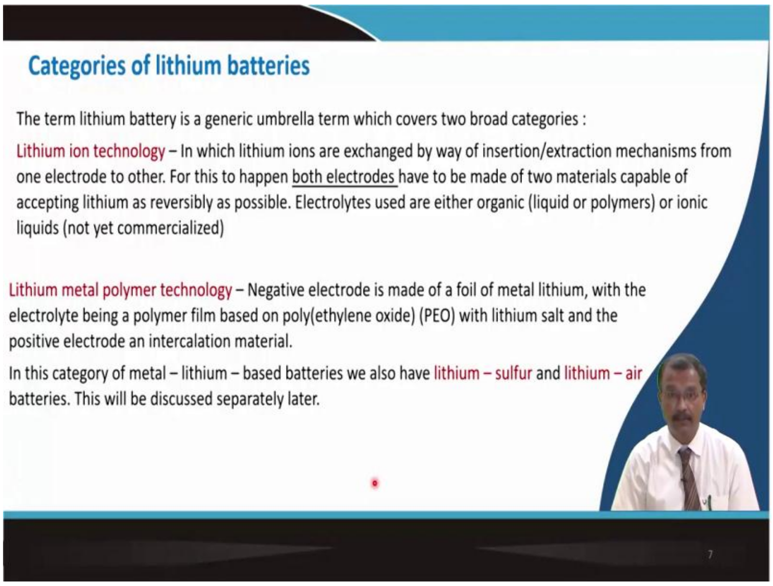

Categories of lithium batteries

The term lithium battery is a generic umbrella term which covers two broad categories :

Lithium ion technology – In which lithium ions are exchanged by way of insertion/extraction mechanisms from one electrode to other. For this to happen both electrodes have to be made of two materials capable of accepting lithium as reversibly as possible. Electrolytes used are either organic (liquid or polymers) or ionic liquids (not yet commercialized)

Lithium metal polymer technology – Negative electrode is made of a foil of metal lithium, with the electrolyte being a polymer film based on poly(ethylene oxide) (PEO) with lithium salt and the positive electrode an intercalation material.

In this category of metal – lithium – based batteries we also have lithium – sulfur and lithium – air batteries. This will be discussed separately later.

So, we can categorize now the lithium batteries. So, this is a generic umbrella term which covers mainly two broad categories – one is lithium ion technology in which lithium ions are exchanged by the way of insertion and exertion mechanism from one electrode to another, with several time I have described.

So, for this to happen both electrodes have to made with two materials which are capable to accept this lithium reversibly as far as practicable. So, it is not only insertion, but it is also it should promote the exertion of the lithium ions back. So, reversibility is important.

Electrolytes, they are used either organic usually for all commercial lithium ion battery liquid electrolyte is used in case of polymer lithium ion battery polymers are used or sometimes ionic liquids are also used as electrolyte. They have certain advantages.

It is not yet commercialized, because of their poor room temperature ionic conductivity. But, otherwise here it is having high flash point higher viscosity is another problem, so that the lithium cannot diffuse that fast. It has some kind of issues, but ionic liquid people are working on now with quite good rigor.

Second one is lithium metal polymer technology. Negative electrode is made out of a foil of metallic lithium. Still you can use metallic lithium. Electrolyte is a polymer film; polymer based film usually polyethylene oxide with lithium salt and positive electrode are usually intercalated material.

So, this since the polymer film is there and there is no liquid electrolyte there so, still it is not that much problematic as compared to pure lithium metal and organic electrolyte.

Other category is metal lithium based battery which I will cover separately. Lithium sulphur we have devoted one module, in fact for lithium sulphur battery which is coming in a big way. And lithium air batteries, that is the ultimate battery that one can make the energy density is almost very near to the gasoline. So, lithium air battery has certain issues we will talk about it later separately in another module.

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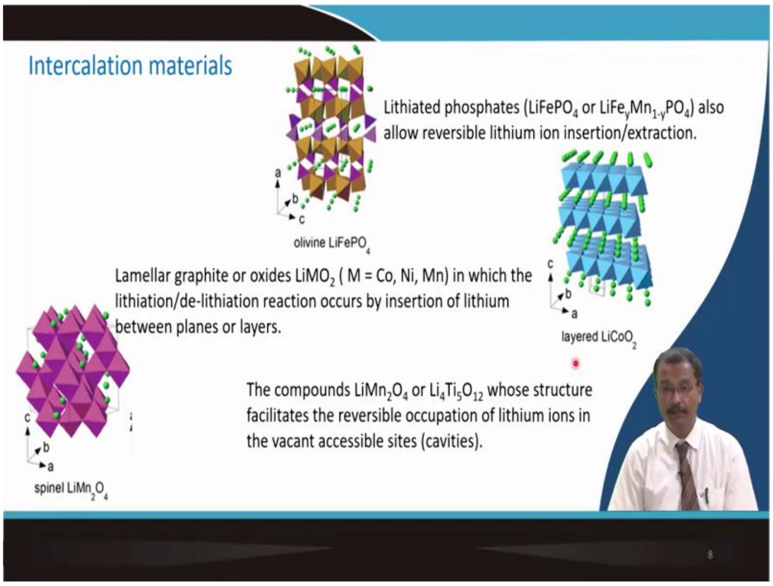

Intercalation materials

Lithiated phosphates ($LiFePO_4$ or $LiFe_yMn_{1-y}PO_4$) also allow reversible lithium ion insertion/extraction.

olivine $LiFePO_4$

Lamellar graphite or oxides $LiMO_2$ (M = Co, Ni, Mn) in which the lithiation/de-lithiation reaction occurs by insertion of lithium between planes or layers.

layered $LiCoO_2$

The compounds $LiMn_2O_4$ or $Li_4Ti_5O_{12}$ whose structure facilitates the reversible occupation of lithium ions in the vacant accessible sites (cavities).

spinel $LiMn_2O_4$

Now, as far as the positive intercalation materials are there. One can use lithiated phosphate LiFePO 4 which is having olivine structure or part of iron can be replaced by manganese. And you know that these are all cheap material as compared to cobalt, nickel.

So, these are cheaper battery and also we will show in other lecture that it gives you a flat voltage profile. So, it allows reversible lithium ion insertion and exertion extraction. So, that is one thing that is in fact, needed. Then lamellar graphite that is used as positive electrode or oxide having this type of formula LiMO 2; where metal could be cobalt, it could be nickel or manganese.

The first commercial battery was this graphite anode material and lithium cobalt oxide as positive electrode material. So, this type of battery it has been commercialized by Sony in 1990, lithiation and de-lithiation reaction that occurs by insertion of lithium between the planes of the layer. So, that you can see here. So, these green things are lithium which is there in between the transition metal octahedra, here as you can see.

Other type of compound is not layered compound, but it is a cage type compound the a b 2 O 4 type of spinel. Already I talked about LiMnO and also talked about lithium titanium oxide in my last lecture. This structure facilitates the reversible occupation of lithium ions in the back end accessible cavities.

So, there are lot of cavities you know the spinel structure, it has tetrahedral void 64 number 8 out of them in normal spinel is filled. So, various free space is available octahedral site is 32 and out of that half are filled. So, lot of void space are accessible and this is also used.

If you take a cubic lattice you know the each centre and the central position they are the octahedral kind of void space. So, you have 12 edges and each of them they are 4 coordinated. So, in all you have 3 plus 1 at the centre 4 octahedral voids. And each body diagonal they have 2 tetrahedral voids. So, you have 4 body diagonals. So, you have total 8 tetrahedral voids.

Now, in case of spinal structure the formula unit this is 8 is the tetrahedral void and 4 is the octahedral void. So, 8 number of this kind of unit cell they forms the formula unit. So, totally you have 64; 64 numbers of tetrahedral voids and 32 numbers of octahedral voids. And as I said one eighth of tetrahedral and half of the octahedral is vacant. So, these are very useful cage type of spinel material which is used both as anode and cathode.

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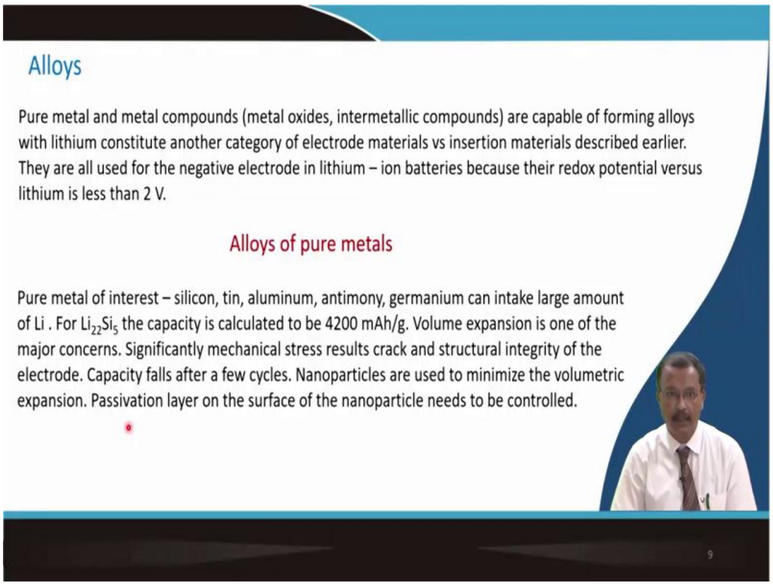

Alloys

Pure metal and metal compounds (metal oxides, intermetallic compounds) are capable of forming alloys with lithium constitute another category of electrode materials vs insertion materials described earlier. They are all used for the negative electrode in lithium – ion batteries because their redox potential versus lithium is less than 2 V.

Alloys of pure metals

Pure metal of interest – silicon, tin, aluminum, antimony, germanium can intake large amount of Li . For $Li_{22}Si_5$ the capacity is calculated to be 4200 mAh/g. Volume expansion is one of the major concerns. Significantly mechanical stress results crack and structural integrity of the electrode. Capacity falls after a few cycles. Nanoparticles are used to minimize the volumetric expansion. Passivation layer on the surface of the nanoparticle needs to be controlled.

Next, we can consider alloy. Pure metal and metal compounds, metal oxides, inter metallic compounds they are capable of forming alloys with lithium. And that constitutes another type of electrode material, and this can be used versus insertion material which I have described earlier.

So, you can form a metal alloy based anode because of voltage again you can calculate back from respective chemical potential lithium ion chemical potential in their anode and cathode and then estimate the voltage. So, you will find that they are quite good, so they can use as negative electrode.

Usually, their redox potential versus lithium is less, but it is still higher as compared to graphite. Graphite is in the range of 0.5, 0.7 electron; 0.5 to 0.7 volt versus lithium. Lithium titanite you have seen that is 1.5, but this kind of alloy this is 2 volts. So, you are basically losing the voltage window of the actual full cell and energy density will also be low.

So, first we will consider alloys of pure metal. So, the metal that is interesting is silicon, it is not really a metal is a semiconducting material. Tin is used, aluminium is used, antimony is used, germanium is used. So, why they are used? Because they can intake large amount of lithium.

See the formula for silicon it is Li 22 Si 5. So, 5 of Si can take 22 lithium. So, it can give the capacity if you calculate from the Faraday law; it is 4200 milliampere hour per gram. And, think of graphite the capacity is only 372 milliampere hour per gram.

But the problem is volume expansion, that is one of the major concern when lithium is alloyed then it forms significant large volume expansion. And that can insert stress and causes structural integrity of the electrode to be dismantled. So, electrode is coated on a current collector. So, if you have this volumetric expansion, then the binder is not able to hold the current collector and electrode material together. So, it causes the delamination.

So, after a couple of cycles when lithium is going in volume expand, then volume reduces, again expand, again reduces couple of cycle you will find that capacity falls down. One of the possible thing to overcome this is to create nanoparticles. And nanoparticles of this alloy they to some extent minimize the volumetric expansion.

The passivation layer on the surface of the nanoparticle of course need to be controlled, because once you are reducing the particle size you are increasing the surface energy. So, it is becoming more reactive to the electrolyte. So, the formation of the so called secondary electrolyte interface layer that you need to control.

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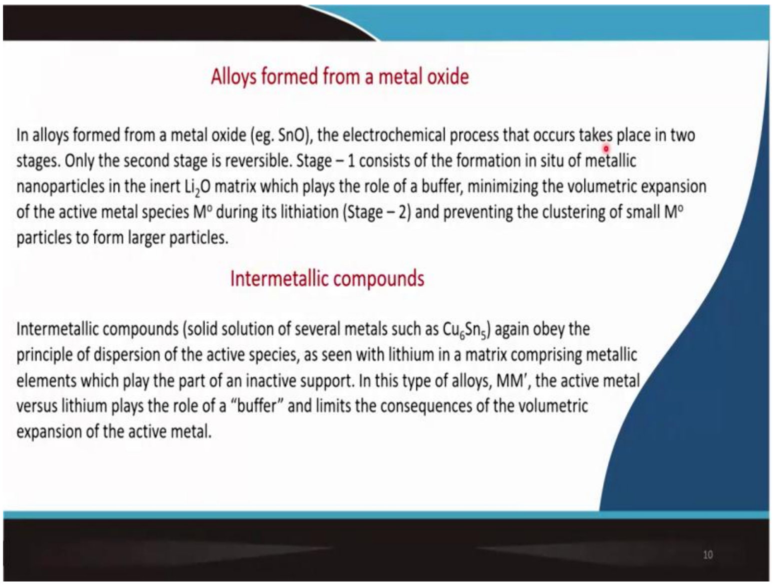

Alloys formed from a metal oxide

In alloys formed from a metal oxide (eg. SnO), the electrochemical process that occurs takes place in two stages. Only the second stage is reversible. Stage – 1 consists of the formation in situ of metallic nanoparticles in the inert Li_2O matrix which plays the role of a buffer, minimizing the volumetric expansion of the active metal species M^o during its lithiation (Stage – 2) and preventing the clustering of small M^o particles to form larger particles.

Intermetallic compounds

Intermetallic compounds (solid solution of several metals such as Cu_6Sn_5) again obey the principle of dispersion of the active species, as seen with lithium in a matrix comprising metallic elements which play the part of an inactive support. In this type of alloys, MM', the active metal versus lithium plays the role of a "buffer" and limits the consequences of the volumetric expansion of the active metal.

It is possible to use metal oxide and interestingly it works in a very different way. The alloy is formed from metal oxide. Say, you take tin monoxide the electrochemical process that occurs takes place in 2-stage; the first stage is reversible sorry first stage is not reversible, but the second stage is reversible.

So, stage 1 consist of the formation of an in situ metallic nanoparticle. So, it forms a in situ metallic nanoparticle. So, it is silica is the this tin is getting dissociated and lithium reacts with oxygen to form Li 2 O. So, inside Li 2 O matrix which actually plays a role of a buffer there are silicon metal particle and it minimizes the volumetric expansion, in the next cycle lithium is coming and it forms alloy with tin.

So, the active metal species it is which is in it is getting reduced as you can see here from plus 2 it is going to 0 oxidation state. And in stage 2 it is lithiation forming the alloy and then it start to form the alloy. So, it also creates some kind of situation where the clustering of this small metal particle they are separated from each other, because of this Li 2 O matrix. So, in that way the volumetric stress that is getting generated it is buffered a bit.

So, intermetallic compound constitute at solid solution type of several metal; that is also another thing that is being tried; copper tin alloy is one example. Again they obey the principle of dispersion of active species; had seen in lithium in a matrix comprising the metallic element which play a part of the inactive support. So, not both of them they alloy form alloy with lithium.

So, if tin forms alloy with lithium, then there will be volumetric expansion. So, the stress will be taken by copper because these are metallic particle having lot of dislocation, the line defects and then the dislocation can move through the slip plane and part of this volumetric strain can be buffered. So, this type of intermetallic compound that is also used as negative material.

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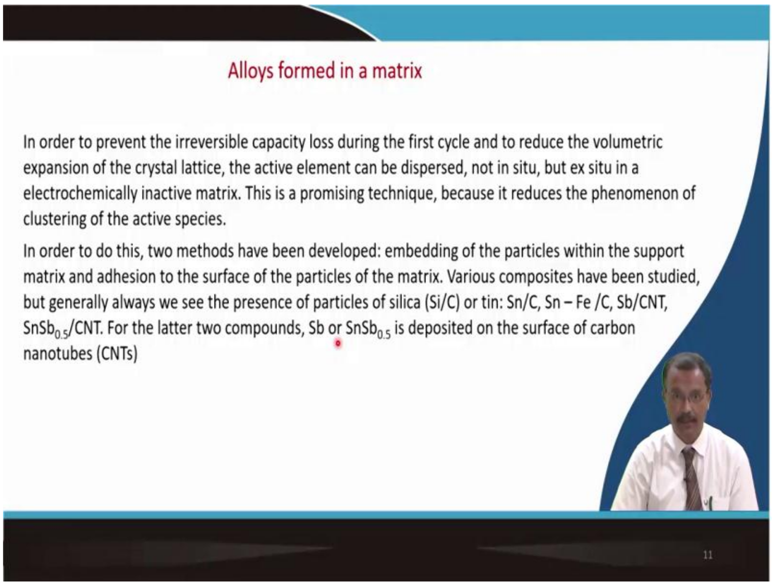

Alloys formed in a matrix

In order to prevent the irreversible capacity loss during the first cycle and to reduce the volumetric expansion of the crystal lattice, the active element can be dispersed, not in situ, but ex situ in a electrochemically inactive matrix. This is a promising technique, because it reduces the phenomenon of clustering of the active species.

In order to do this, two methods have been developed: embedding of the particles within the support matrix and adhesion to the surface of the particles of the matrix. Various composites have been studied, but generally always we see the presence of particles of silica (Si/C) or tin: Sn/C, Sn – Fe /C, Sb/CNT, SnSb$_{0.5}$/CNT. For the latter two compounds, Sb or SnSb$_{0.5}$ is deposited on the surface of carbon nanotubes (CNTs)

So, in order to prevent the irreversible capacity loss during the first cycle and to reduce the volumetric expansion of the crystal lattice, the active element they can be dispersed, not in situ, but ex situ in an electrochemically inactive matrix. This is a promising technique, because it reduces the phenomena of clustering of the active species the small metallic species.

In order to do that two method basically have been developed – the number one is embedding the particles within the support matrix and adhesion to the surface of the particle of the matrix. So, proper adhesion is required. So, some of the composite that has been studied are silica; silica and carbon composite which I will talk about later on usually silicon dioxide is used and then it is reduced to form silica in a carbon nanotube kind of thing.

Or tin; tin is another example tin carbon or tin iron carbon or antimony in CNT or tin antimony in CNT. This latter two compounds tin and sorry, antimony or tin antimony, this is deposited on the surface of a carbon nanotube to forms this kind of anode material.

So, all this is done to ensure that alloy formation takes place lot of lithium intake is there. At the same time you will have to stop the volumetric expansion, so some kind of buffer things needs to be there. So, either it is in situ in case of oxide or it is externally you add this in carbonaceous material to form this negative electrode.

Again I will come back to this when we will study the case study particular case we will analyse.

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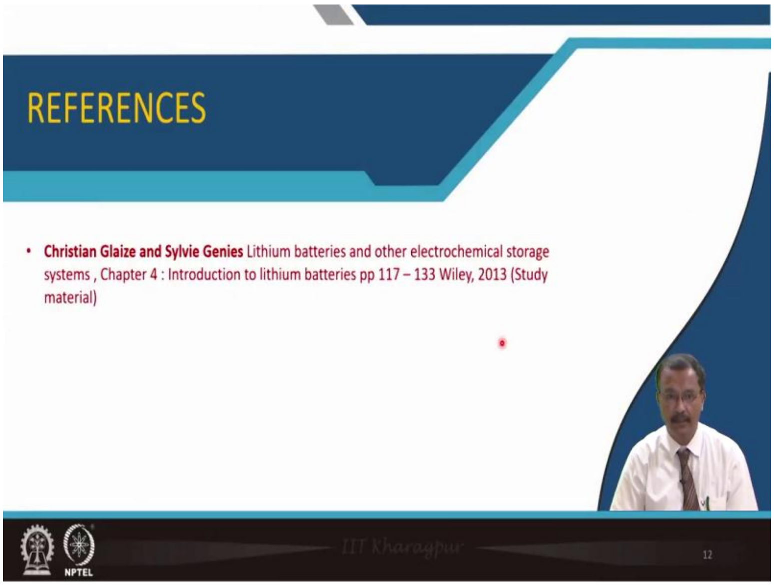

REFERENCES

- **Christian Glaize and Sylvie Genies** Lithium batteries and other electrochemical storage systems , Chapter 4 : Introduction to lithium batteries pp 117 – 133 Wiley, 2013 (Study material)

So, the reference that is used is the book by Christian Glaize and Sylvie Genies, one of the good book which has lot of information. So, that is in fact, one of the major text book that I have used for this course. And this is page number 117 to 133 it is a Wiley book that you can consider, you can read to clarify these ideas.

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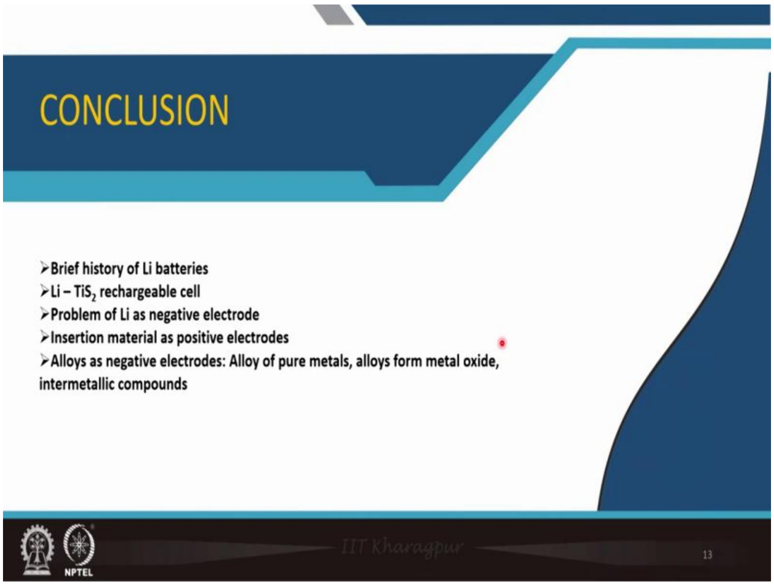

CONCLUSION

- Brief history of Li batteries
- Li – TiS_2 rechargeable cell
- Problem of Li as negative electrode
- Insertion material as positive electrodes
- Alloys as negative electrodes: Alloy of pure metals, alloys form metal oxide, intermetallic compounds

So, I have introduced in this particular class; brief history of lithium batteries, lithium titanium disulfide rechargeable cell, then the problems of lithium as negative electrode mainly dendrite formation, insertion material as positive electrodes.

So, couple of insertion material like olivine type or layered oxide intercalation type or spinal oxide materials have been considered. And then alloy as negative electrodes, so alloy of pure metals alloy of metal oxide and inter metallic compounds.

Thank you for your attention.