

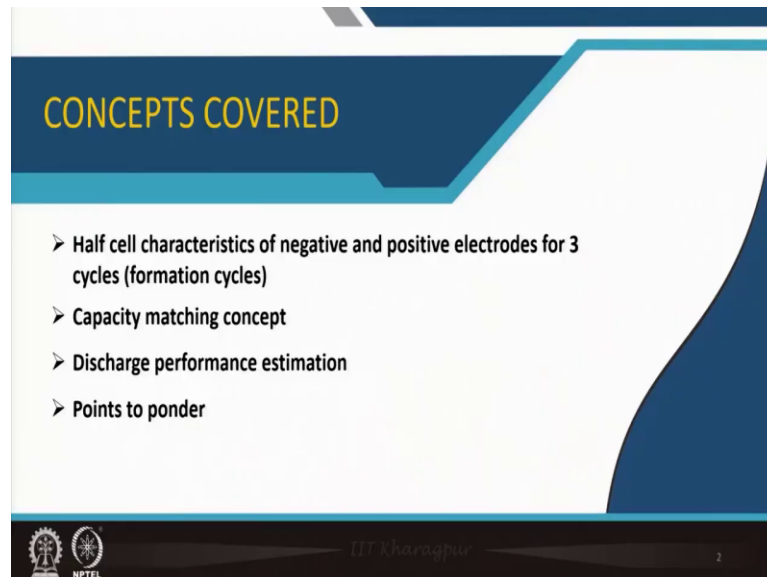
**Electrochemical Energy Storage**  
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**Module - 05**  
**Characteristics of commercial lithium ion cells**  
**Lecture - 22**  
**Principle of Operation of Commercial Cells**

Welcome to my course Electrochemical Energy Storage and we are now in module number 5 where I am describing Characteristics of commercial lithium-ion cells. And this is lecture number 22 where we will be talking about the Principle of Operation of Commercial Cells.

Now, already in the last lecture, I have introduced the concepts that is basically taken care of while fabricating the commercial cells for lithium-ion battery related applications.

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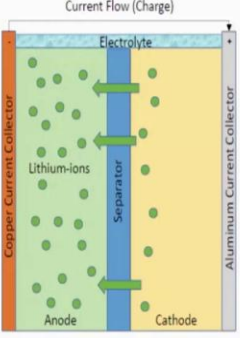
And in this particular lecture, we will talk about initially the half-cell characteristics for both negative as well as positive electrode materials. And usually, roughly 3 numbers of cycles charge and discharge that is adopted, I will tell why and this is part of the formation cycles. And then, based on the data, we again will relook at the capacity matching concept because most of the instances, the positive and negative

electrodes, they have different specific capacities; so, how to control this capacity matching that will be introduced.

Then, discharge performance estimation will be described and there are certain things that should trigger the thinking in you after taking so many lectures whatever I have covered so far. And this points to ponder is the final things that I will introduce.

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**Commercial Li ion cells: General characteristics**



The diagram illustrates the internal structure of a commercial Li-ion cell. It shows a central electrolyte region containing a separator. On the left is the anode, which is connected to a copper current collector. On the right is the cathode, which is connected to an aluminum current collector. Green dots representing lithium ions are shown moving from the cathode to the anode during a charging event and from the anode to the cathode during a discharging event. Arrows indicate the direction of current flow (charge) through the external circuit and the movement of lithium ions through the electrolyte.

**Charging event** – Lithium ions within the cathode are transferred through an electrolyte medium into the anode.  
**Discharging event** – Lithium ions being transferring through an electrolyte medium from anode into cathode.

For NiMh battery pack with 350 V may require 292 cells to achieve that voltage ( $350V/1.2V = 292$  cells). Whereas a lithium ion based battery pack would require about 98 cells to achieve the same voltage ( $350V/3.6V = 98$  cells)

Lower rate of self discharge (1 -5% per month).  
Reversible capacity loss is regained during cycling.

Much better cycle life 1000 cycles using 100% DOD. For 80% of its total useable energy we can run several thousand cycles.

So, again, you can have this commercial lithium-ion cells and in commercial lithium-ion cells, you know by this time; what is the actual operation that is going on inside an individual cell. So, here, there is a charging event where lithium ions which stays in the cathode or positive material, they are transferred through this electrolyte-soaked separator.

And in most of the cases, they are intercalated for intercalation related negative electrode materials. And during the discharge event, this lithium ions, they are transferring from this negative electrode materials back to the positive electrode material.

So, if you consider a nickel metal hydride battery pack and if you want to have a 350 volt voltage from this battery pack if individual cells you know that the voltage is 1.2 volt so, you need 292 cells, but if you replace it with lithium ion based battery

pack that will have typically 3.6 volt nominal voltage. So, you are ending up with much lower number of cells, 98 cells will serve the purpose for you to get 350 volt battery pack. So, you can pack lot of energies in a small space. So, the volumetric energy density of this battery will certainly be higher.

Another advantage of lithium-ion cells are there if you put it in charge condition, the selfdischarge is only 1 to 5 percent per month so, you can charge the battery and leave it for a month or so, very nominal capacity drop you will notice.

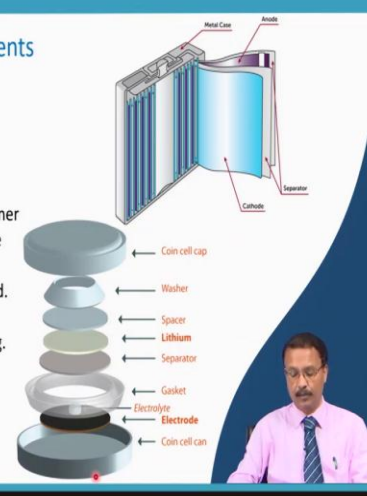
And apart from that, this lithium ion cells they have much much better cycle life about 1000 cycles using almost 100 percent depth of discharge, because you can discharge it up to a certain specified voltage limit that is possible. And typically, for a good quality cell, 80 percent of the total usable energy we can get after running several 1000 cycles.

So, it is really advantageous for us to use lithium-ion cell instead of the other chemistry like nickel metal hydride or nickel cadmium lead acid that will offer slightly higher voltage about 2 volt, but still as far as the energy density is concerned, lithium ion batteries they are much much superior off than the existing technologies.

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**Commercial Li ion cells: Basic components**

- Aluminum foil coated with composite cathode
- Copper foil coated with composite anode material
- Separator – PP or PE, between anode and cathode.
- This forms the jellyroll which is inserted into the container or housing (Metal can, plastic enclosure, metal foil type pouch)
- Into this assembly is then injected the electrolytic liquid.
- The enter assembly is then hermetically sealed and is ready to move into the next stage of cell manufacturing.



The diagram illustrates the internal structure of a coin cell battery. It shows a cross-section of the cell with labels for the Metal Case, Anode, Cathode, and Separator. Below this, a detailed exploded view of the coin cell assembly is shown, with labels for the Coin cell cap, Washer, Spacer, Lithium, Separator, Gasket, Electrolyte, Electrode, and Coin cell can. A small inset image shows a person in a pink shirt and tie, likely the presenter.

Coin cell to test the electrodes

So, here I have shown different types of shape of the battery, cylindrical, you know about the pouch cell now, in is a prismatic cell as you can see that it is a rectangular shape so, packaging is a bit different and cell construction is almost similar to that of the pouch cell which I will be describing today.

So, aluminum foil that is coated basically with the composite cathode and copper is taken for anode material current corrector and the choice is basically as you know that is basically dictated by the corrosion, inhibition at the selected voltage range. And also, the cost is another factor and the density of the metal, copper is still heavier as compared to aluminum, but density is also another concern, but we are happy with copper foil.

Separator is usually polypropylene or polyethylene based material porous which is kept in between anode and cathode that basically forms a jelly roll which is inserted into the housing. That housing could be prismatic one or it could be a metal can or it could be a plastic enclosure what we will describe in case of the pouch cell.

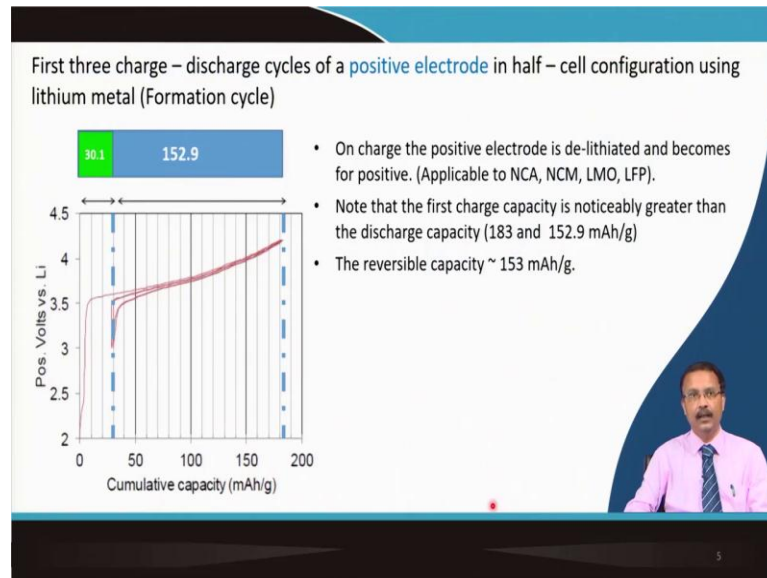
And then in the assembly, in a controlled oxygen and moisture environment, you fill it up with the electrolyte, soak it with the electrolyte so that the separator and also, part of the positive and negative electrode, they are properly soaked by this electrolyte. So, vacuum ceiling or vacuum based electrolytic filling that is required so that it is eventually or uniformly, distributed inside the cell.

Then, the entire assembly you will have to get disconnected from the ambient because if you know that if moisture is present, then moisture react with the salt which is LiPF<sub>6</sub> and it will create hydrofluoric acid and this hydrofluoric acid is corrosive so that will deteriorate the cell performance so, it is hermetically silt and this is ready to move to the next stage of cell manufacturing.

Now, to test the electrode material in half-cell configuration, we usually use this coin cell kind of configuration, where you can see the electrode is coated, this is positive electrode. Then there is a separator which is soaked with electrolyte and then, you have gasket, you will have to seal the cell, then you have a separator that is basically soaked here the separator is there.

Then in half-cell, you know that you will have to use lithium foil. Then there is a spacer which will basically absorb the space which is left behind to make it more tight, tighter the spacer is required, the washer is required and then, you have a top can and everything is crimped to make this kind of bottom cell which we usually use for electrode electrochemical characterizations.

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Now, in case of a positive electrode, first you will have to do the coating etcetera and prepare the electrode. And in coin cell configuration, you will have to do at least three charge discharge cycles depending on the electrode. If you have a good quality of electrode, three is sufficient. So, first three charge discharge cycles of a positive electrode material in a half-cell configuration using lithium metal so, this we call formation cycles.

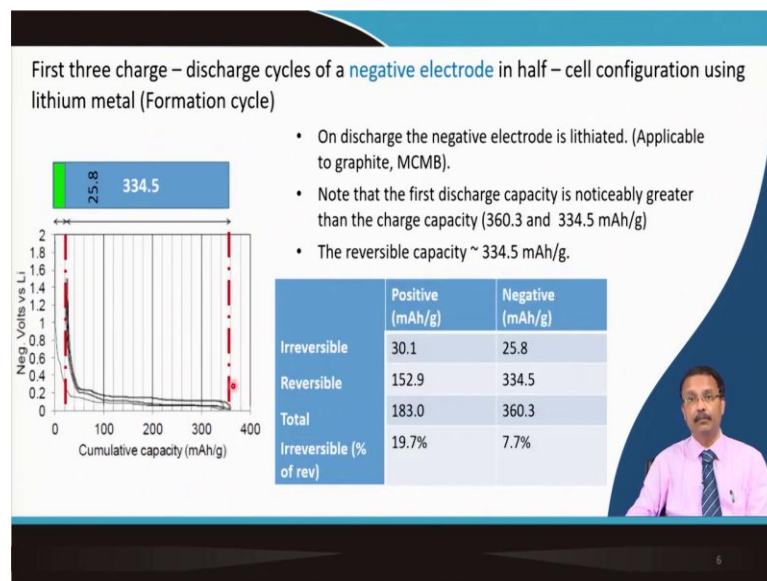
So, you can understand from this curve initially, this is getting charged and then eventually, it is getting discharged, then again it is getting charged and eventually, you can also discharge it.

So, once you charge the first time, this is basically de-lithiated, lithium is getting extracted and it becomes more positive because this transition metal cation they are getting oxidized because lithium is going out from the system. So, plus 2 valent is oxidized to plus 3, plus 3 is oxidized to plus 4 that you know by this time and the same thing happens for LMO or LFP.

So, the first charge capacity that you can see it is noticeably greater as compared to the discharge capacity. You are getting here 183 and then, once you do the discharge and again charge and just follow it, then you will see the capacity is stabilized at around 152.9 milliampere hour per gram which you can easily estimate from the coin cell electrochemical characteristics.

So, we will term that this is the reversible capacity for the cathode material and some part of the capacity that is not reversible, it is about 30.1 in this case milliampere hour per gram. And that is basically happening because of several factors that lithium is coming out, crystal structure changes and then, lithium is not finding the exact place where it was there before. So, that reduces part of this capacity which you cannot get it back so, this is irreversible capacity.

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The same thing happens for the negative electrode material in half-cell configuration. So initially, this is applicable for graphite and MCMB kind of thing, from the voltage you can identify that this is MCMB or graphitic negative electrode materials.

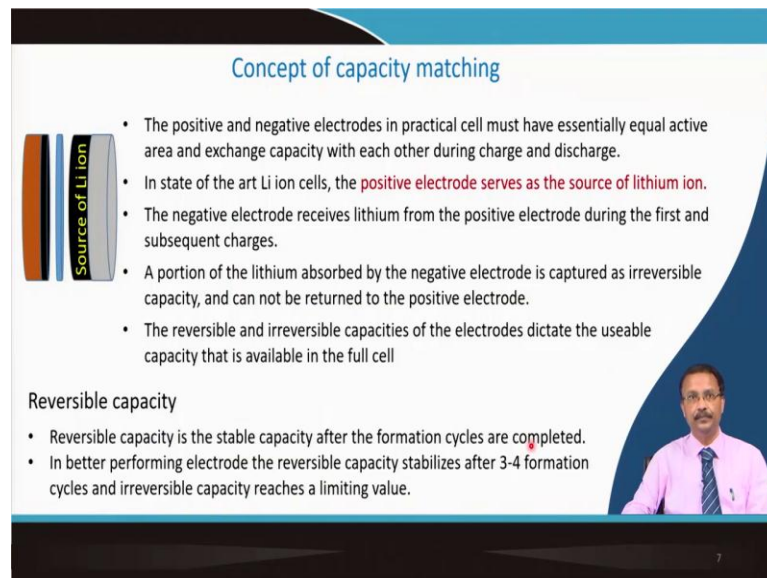
So, once the positive electrode is charged that means, lithium is coming out so, if you put against a lithium metal plate, then graphite ion will first get discharged. And you can see that the this discharge capacity is about 360 milliampere hour per gram. And again, you do several charge and discharge typically, three numbers of cycle,

you see now the capacity which is reversible it is 334.5 according to this particular experimentation. So, I will term the reversible capacity is 334.5 milliampere hour per gram.

So now, I know for positive electrode, irreversible capacity is 30.1, for negative electrode, it is roughly about 25.8. Reversible capacity for the positive electrode is 152.9 and for negative it is 334.5.

So, total capacity here is about 183 and total capacity for the negative electrode is about adding this one and this one where this is your irreversible capacity, this is coming around 360.3. So, total percent of irreversible capacity with respect to the reversible capacity is larger here 19.7 as compared to the negative electrode, which is 7.7 percent, you can work it out.

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**Concept of capacity matching**

- The positive and negative electrodes in practical cell must have essentially equal active area and exchange capacity with each other during charge and discharge.
- In state of the art Li ion cells, the **positive electrode serves as the source of lithium ion**.
- The negative electrode receives lithium from the positive electrode during the first and subsequent charges.
- A portion of the lithium absorbed by the negative electrode is captured as irreversible capacity, and can not be returned to the positive electrode.
- The reversible and irreversible capacities of the electrodes dictate the useable capacity that is available in the full cell

**Reversible capacity**

- Reversible capacity is the stable capacity after the formation cycles are completed.
- In better performing electrode the reversible capacity stabilizes after 3-4 formation cycles and irreversible capacity reaches a limiting value.

Source of Li ion

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Now, there is a concept called capacity matching. The positive and negative electrode in practical cell not in half-cell, when you are using graphite and the positive electrode and construct the full cell. They must have essentially equal active area so, the active area should be same more or less same so, the construction of cell will be something like that so that active area is same. And the exchange capacity with each other during charge and discharge that will be beneficial if you have equal active area.

Now, in case of state of art lithium-ion batteries, the positive electrode that is the source of lithium ion and through electrolyte, this lithium is conducting and that is getting basically intercalated to graphite.

So, the source of lithium is cathode so, that source will have to be properly utilized, it is not like half-cell that you have enormous source of lithium because you are using a lithium plate. So, whenever there is a dearth of lithium, it can get from this half-cell, this this negative lithium metal foil, but this is not the case in case of full cell.

And the negative electrode that receives the lithium from positive electrode during the first and subsequent charges. That portion of this lithium that is absorbed by the negative electrode and that is captured as irreversible capacity and cannot be returned to the positive electrode which already I have explained.

And the reversible and irreversible capacity of the electrodes that dictate the usable capacity that is available in the full cell. So, if you consider the reversible capacity that basically is the stable capacity after the formation cycle are completed. So, this one, this much capacity will be getting.

In a better performing electrode, the reversible capacity is stabilized within 3 to 4 formation cycle, but if your quality of the electrode material is not that great, then it takes some time so, you will have to continue still you get a constant reversible capacity that you must take into account. But usually, if you have a good quality electrode, your cell construction is good, then you can expect within three cycles, you will get a reasonably good reversible capacity.



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The slide is titled "Concept of capacity matching" and discusses "Irreversible capacity". It contains a list of six bullet points. A small video inset in the bottom right corner shows a man in a pink shirt and tie speaking.

**Concept of capacity matching**

**Irreversible capacity**

- Irreversible capacity contributes to the total charge capacity that is absorbed by the electrode in the initial (formation) cycles.
- In case of the positive electrode, the extraction of lithium in the first charge induces changes to the crystal structure, making it impossible for the same amount of lithium to be re-inserted in the subsequent discharge cycle. Hence, the quantity of lithium that is removed can not be replaced.
- At the negative electrode, the initial transfer of lithium reduces the potential and induces electrochemical reactions (reduction) with the electrolyte. The reduction products are electrochemically inactive species that comprises the solid electrolyte interphase (SEI)
- For commercial cells it is assumed that the capacity performance of each electrode is the same as in half cells
- Allowance for the irreversible capacity forms an important consideration in the capacity balance of the electrode in full cell.

Now, in case of irreversible capacity that contributes the total charge capacity that is absorbed in the electrode in the initial formation cycle so, that is there as a date capacity. In case of positive electrode, extraction of the lithium in the fast charge that as I told induces some kind of change in the crystal structure, making it almost impossible for the same amount of lithium will re-inserted in the subsequent discharge cycle. Hence, the quality sorry quantity of lithium that is removed that cannot be replaced and that is why this irreversible capacity is there.

In the negative electrode, the initial transfer of the lithium reduces the potential as you have seen. And the reduction of the products electrochemically produce the inactive species and that basically comprises the solid electrolyte interface, SEI layer we have already talked about and that is more meaningful when you are considering the negative electrode.

Now, for the commercial cell, it is assumed that the capacity performance of the each cell sorry, each electrode is same in the half-cell. So, allowance of this irreversible capacity which are of different percentage as you have seen that is an important consideration while you do the capacity balance of the electrode in the full cell.

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**Concept of capacity matching**

Capacity ratio consideration

- Based on the room temperature half-cell performance, let us illustrate a sample calculation to make a 35 Ah cell.
- For 35 Ah positive reversible capacity, the irreversible capacity of the positive electrode is  $(35 \text{ Ah} \times 0.197) = 6.9$
- Total positive capacity is  $35 + 6.9 = 41.9 \text{ Ah}$**

	Positive (mAh/g)	Negative (mAh/g)
Irreversible	30.1	25.8
Reversible	152.9	334.5
Total	183.0	360.3
Irreversible (% of rev)	19.7%	7.7%

- Positive capacity should always be a bit lower than negative electrode capacity to avoid lithium electroplating (prone to dendritic growth). Let us assume  $P/N = 0.909$ . Hence negative capacity is  $41.9/0.909 = 46.09 \text{ Ah}$
- Let  $x$  be the reversible capacity of the negative electrode. Hence  $x \times 0.077 =$  irreversible capacity.
- $x + 0.077x = 46.09$ . Hence reversible capacity is  $46/1.077 = 42.79 \text{ Ah}$  and irreversible capacity is  $42.79 \times 0.077 \text{ Ah} = 3.30 \text{ Ah}$



Now, let us take an example. So, capacity ratio you can basically estimate. This is an important criteria and I have another set of calculation based on our own cylindrical cell calculations, that is not included here but the concept you will get maybe in the assignment or some other platform we will discuss it in more details. So, but this is sufficient.

Based on the room temperature half-cell performance, let us illustrate the sample calculation to make a 35 ampere hour cell. So, that kind of capacity this cell is having. So, for 35 Ampere hour positive reversible capacity, irreversible capacity of the electrode is multiplied to 19.7 percent so, about 6.9 milliampere sorry Ampere hour that is lost as irreversible capacity.

So, the total positive capacity that you initially want for is 35 plus 6.9 and the same thing is true for positive electrode material.

So, here, you know the positive electrode we keep little bit lower capacity why; because the source of lithium is from positive electrode. If it is not totally consumed in the negative electrode in terms of intercalation for graphite, then it will electroplate and form the dendrite structure so, it is problematic. So, therefore, positive is to negative ratio that is kept about 90 percent. So, negative capacity is coming about 46.09 based on this right. So, this is coming.

Now, you will have you know that what is the irreversible capacity so, taking into that, the irreversible capacity you will have to do this calculation to get this irreversible capacity and the total capacity is the reversible capacity and irreversible capacity. So, if you solve this one, then you will get about 42.79 Ampere hour that is the irreversible capacity sorry; that is the total capacity and out of that, irreversible capacity is only 3.30 Ampere hour.

So, now, you have taken consideration of the reversible capacity which is same for both the electrodes based on your half-cell data where you estimated the irreversible and reversible part of the capacity in half-cell configuration.

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**Concept of capacity matching**

6.90

35 Ah Positive

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3.30

42.79 Ah Negative

- The positive reversible capacity limits the useable window of operation for the negative electrode to the 35 Ah region shown by the arrow.
- The limited positive capacity prevents negative from becoming fully discharged.

Maximum state of charge for the negative electrode  $(6.90 + 35 - 3.30)/42.79 = 90.2\%$   
 Minimum state of charge for the negative electrode  $(6.90 - 3.30)/42.79 = 8.4\%$

	Positive	Negative
Reversible capacity (Ah)	35	42.79
Specific capacity (mAh/g)	152.85	334.50
Active material (g)	229	127.9

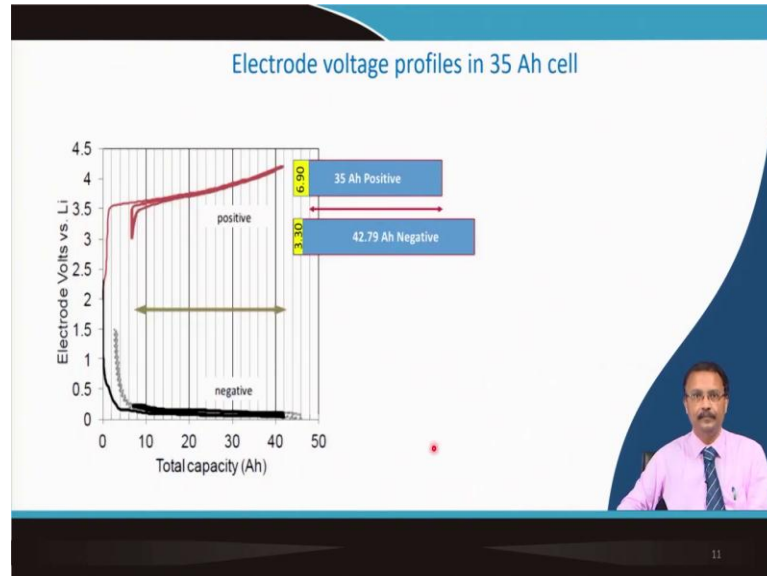


So, here is the actual thing. So, you have 35 Ampere hour positive that is needed and this is a dead mass 6.9 and here, the dead mass is 3.30 and you have considered 90 percent of this thing will be there as compared to this one so that there is no excess lithium for electroplating. So, this much amount you are consuming. So, this kind of cell is called the; positive electrode influenced type of cell.

So, maximum state of charge for the negative electrode you can estimate, this is about 90.2 percent and minimum state of charge for the negative electrode you can estimate from the irreversible capacity is about 8.4 percent. If you summarize it, reversible capacity for positive is 35, negative is 42.79, specific capacity you can calculate now 152.85 knowing the weight and negative is 334.50 and active material

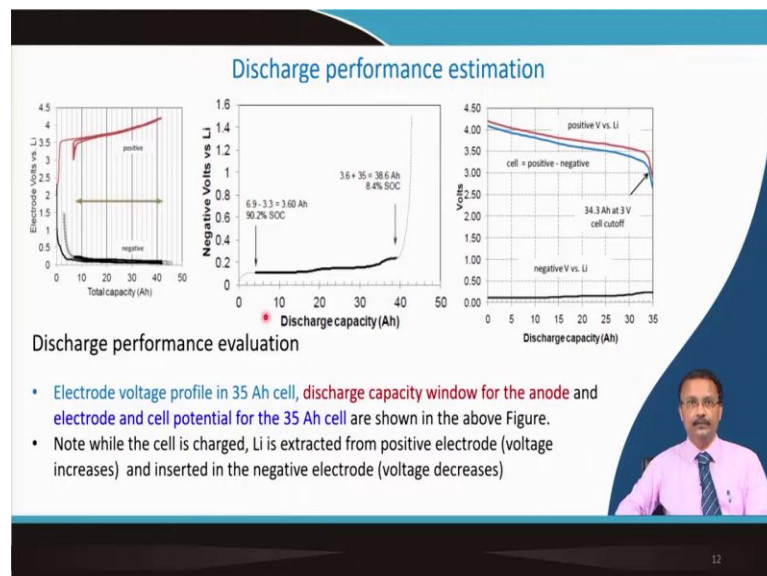
you will have to know or getting this. So, you should know this first, so that you can calculate this, you should know this first so that you can calculate this one.

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So, here is the actual case once again. So, this is the initial charge of the positive electrode, then this is the reversible part, this is the initial charge for the, initial discharge for the negative electrode and out of that, this part is reversible and you are now considering only this part for a capacity balance. So, you are confined to this type of capacity estimation.

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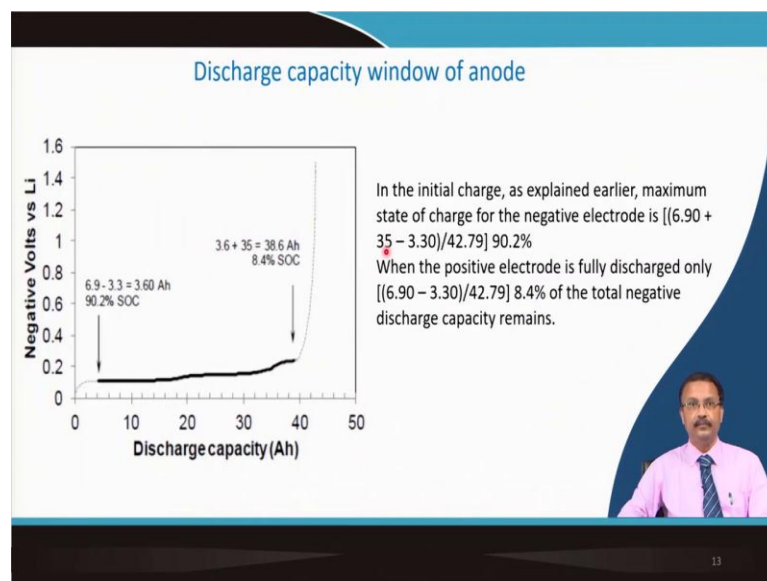


I have again the performance estimation I have shown it here so, this is the electrode voltage profile of a 35 Ampere hour cell. The discharge capacity window for the anode and the electrode and cell potential for 35 Ampere hour cell all these things are shown in this figure. So, this is for your negative electrode, this is for your positive electrode. So eventually, you are taking care of only this much amount of the discharge capacity which is roughly 35 and not taking into account of this part as well as this part.

Now, if you just look at the discharge profile of this half-cell, you can see the full cell configuration you have almost gotten 35 Ampere hour, this is from an experimental data and this red and black is the half-cell characteristics within this voltage window. So, eventually, you will end up with slightly lower capacity about 34.3 Ampere hour when you discharge it up to 3 volt.

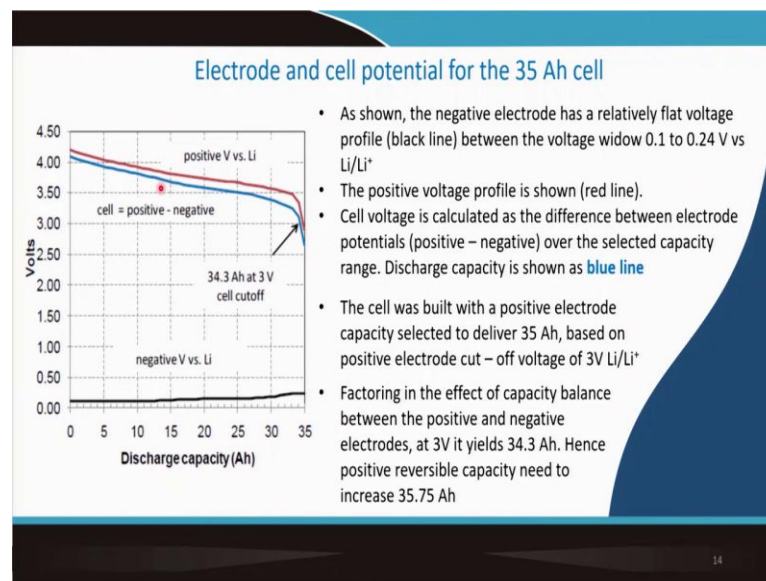
So, you will have to note now that in case of full-cell, when the cell is charged, then lithium is extracted from the positive electrode and voltage is increased, but when it is discharged, then the lithium is inserted into the positive electrode. So, according to the Nernst equation or the other profile calculation we described, you see that this is reduced and this one is slightly increased, but we have cut off these two just to get rid of the detrimental effect that it may have in the cell.

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So, the discharge capacity window of an anode as I have explained earlier, the maximum state of charge for the negative electrode you can calculate, it is about 90.2 percent and when the positive electrode is fully discharged so, only 8.4 percent of the total negative discharge capacity is remaining; because you know that we have intentionally kept the p by n ratio is lowered about 90 percent to avoid the lithium electroplating.

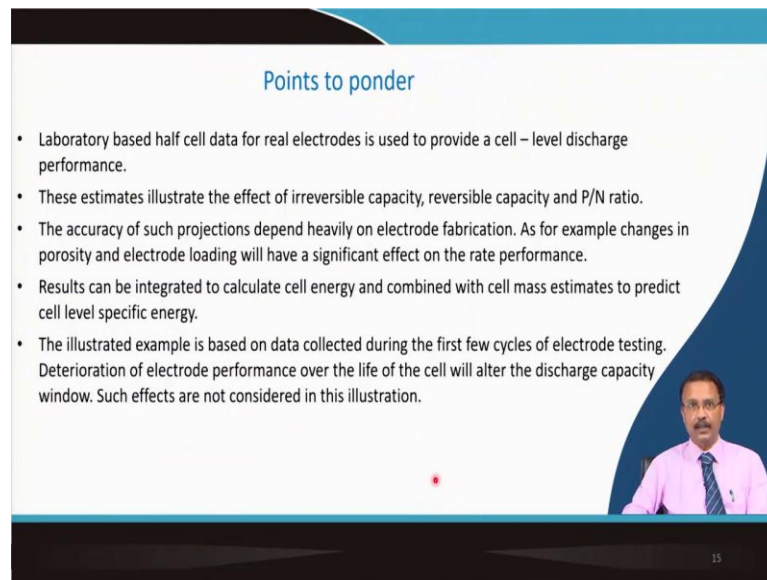
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So, as shown, the negative electrode has a relatively flat voltage profile that is this black line between this voltage 0.1 to 0.24 volt. The positive voltage profile is shown in the red line, the cell voltage is calculated as the difference between the electrode potential which is positive minus negative over the selected capacity range; so, discharge capacity is shown in the blue line. And the cell was built with positive electrode capacity to deliver 35 Ampere hour on positive electrode cut off voltage about 3; 3-volt.

So, factor; the fact the capacity balance between positive and negative electrodes at 3 volt that actually yields you little bit smaller voltage than this red one so, slight change 34.3 Ampere hour. So, the positive reversible capacity need to be increased to 35.75 Ampere hour instead of exactly 35 if you want to have 35 Ampere hour in your full cell. So, accordingly, you will have to increase the active mass of the positive electrode to get that kind, this kind of capacity.

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**Points to ponder**

- Laboratory based half cell data for real electrodes is used to provide a cell – level discharge performance.
- These estimates illustrate the effect of irreversible capacity, reversible capacity and P/N ratio.
- The accuracy of such projections depend heavily on electrode fabrication. As for example changes in porosity and electrode loading will have a significant effect on the rate performance.
- Results can be integrated to calculate cell energy and combined with cell mass estimates to predict cell level specific energy.
- The illustrated example is based on data collected during the first few cycles of electrode testing. Deterioration of electrode performance over the life of the cell will alter the discharge capacity window. Such effects are not considered in this illustration.

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So, the points that you need to ponder about is that the laboratory-based half-cell data for real electrode is used to provide a cell-level discharge performance. So, you will have to do if you are interested to make a full cell in various configuration not only coin cell, but in cylindrical or pouch or prismatic, you will have to do that and this estimates illustrate the effect of irreversible capacity, reversible capacity and the positive and negative electrode mass ratio.

The accuracy of such projection that depends heavily on the electrode fabrication. For example, changes in porosity, so you will have to see the microstructure of the respective electrode after you do the tape cast. Electrode loading, they will have significant effect on the rate performance.

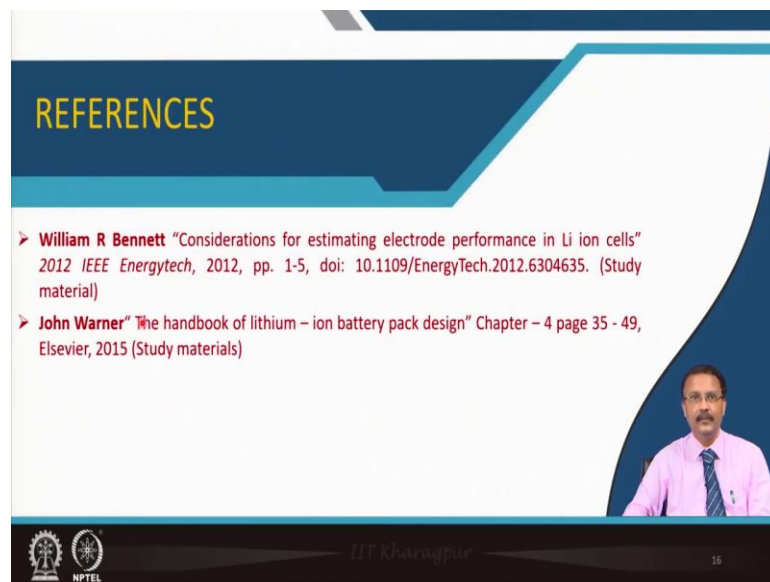
So, discharge capacity will getting at a particular low current rate, but if you increase the capacity sorry increase the rate, then whether it will be followed or not that will depend on the microstructure. So, lot of processing you will have to do in the electrode fabrication, I will explain it later.

This results can be integrated to calculate the cell energy and combined with the cell mass estimates to predict the cell level specific energy. That is already you know because in lecture number 21, I showed you how to estimate this discharge energy, energy density and power density etcetera.

So, the example that I have cited is based on the data collected during first few cycles of the electrode testing. So, once the electrode performance is deteriorated with cycle, then all this reversible and irreversible estimation, pre-estimation whatever we have done to construct the full cell, that will get jeopardized.

So, you will have to ensure that the electrode that you are making after repeated charge and discharge cycles that will offer you same kind of electro chemical performance so, that is very important. So, this is just as a guideline, but not necessarily only three forming cycle will give you enough flexibility to make hundred numbers of cells by this calculations. So, it is indeed a bit tricky.

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The slide is titled "REFERENCES" in yellow text on a dark blue background. It contains two references listed in red text:

- William R Bennett "Considerations for estimating electrode performance in Li ion cells" 2012 IEEE Energytech, 2012, pp. 1-5, doi: 10.1109/EnergyTech.2012.6304635. (Study material)
- John Warner" The handbook of lithium – ion battery pack design" Chapter – 4 page 35 - 49, Elsevier, 2015 (Study materials)

In the bottom right corner, there is a small video inset showing a man in a pink shirt and tie speaking. At the bottom of the slide, there are logos for NPTEL and IIT Kharagpur, along with the number 16.

So, the reference for this particular lecture is very very well written by this paper from NASA group and this is your study material. This is a paper which you can download and the book by John Warner, Handbook of lithium-ion back pack design, this is I told this is an excellent book chapter 4 and page numbers are given.

Please do read it and do this calculation whatever I have showed with your own hand so that you get a fill about this. It would have been better if you can come in the laboratory and exercise it and make your own cell, but virtually, it may be difficult. But this will actually be practiced and well understood to become a good cell manufacturer.



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**CONCLUSION**

- Half cell characteristics of negative and positive electrodes for 3 cycles (formation cycles)
- Capacity matching concept
  - Reversible capacity
  - Irreversible capacity
  - Capacity ratio consideration
- Discharge performance estimation
  - First charge capacity
  - Discharge capacity
- Points to ponder

The slide features a blue and white geometric design. A small video inset in the bottom right corner shows a man in a pink shirt and tie. The footer includes the IIT Kharagpur logo, the NPTEL logo, and the slide number 17.

So, in this particular lecture, half-cell characteristics of negative and positive electrodes for 3 cycles there is a formation cycle, what are their implications that I have talked about. Then the capacity matching concept taking into consideration of the reversible capacity, irreversible capacity and the capacity ratio consideration that has been introduced.

Then, discharge performance evolution, fast charge capacity and the discharge capacity, how to take the capacity which is exactly in between. So, accordingly, the charge and discharge voltage, that window you will have to play with that. And there are certain things that you should always keep it in mind, so that is enlisted in points to ponder.

Thank you for your attention.