Electrochemical Energy Storage

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Module - 11
Li - Air batteries
Lecture - 43
Limitations of Li - Air Batteries

Welcome to my course Electrochemical Energy Storage and this is module number 11, where we are discussing Lithium Air Batteries. This is lecture number 43, where we will basically talked about; basically we will talk about the Limitations of Lithium-Air Batteries. In the previous two lectures, I outlined some of the difficulties. So, we will consolidate it and describe it in details in this particular lecture.

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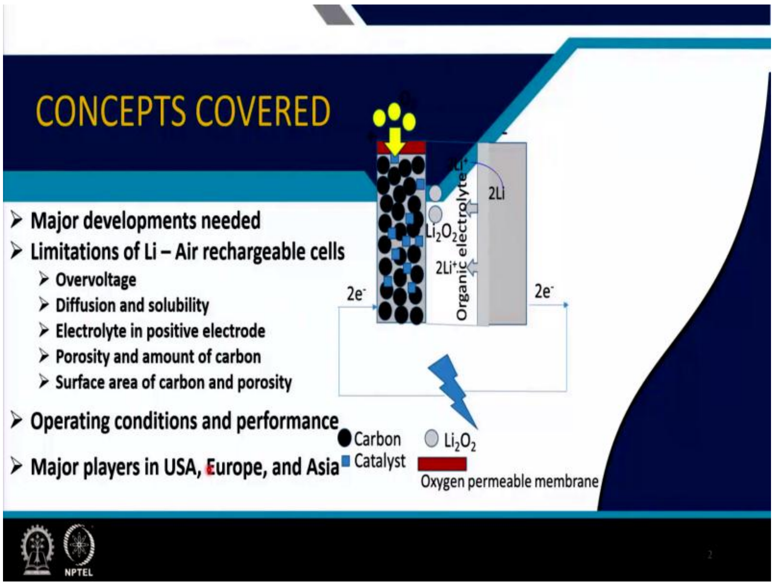

CONCEPTS COVERED

- Major developments needed
- Limitations of Li – Air rechargeable cells
  - Overvoltage
  - Diffusion and solubility
  - Electrolyte in positive electrode
  - Porosity and amount of carbon
  - Surface area of carbon and porosity
- Operating conditions and performance
- Major players in USA, Europe, and Asia

So, as you can now understand that the structure is quite straight forward, that you need to air to pass through this carbonaceous electrode material and catalyst is there to have this oxygen reduction reaction efficiently. And, on the other side the negative electrode pure lithium is used and depending on your aqueous electrolyte or the organic electrolyte; particularly in case of aqueous electrolyte, you do need a protective layer.

And, first the discharge reaction takes place, where eventually Li 2 O 2 forms and during charging Li 2 O 2 gets dissociated, very straight forward reaction mechanism, but lot of problems there involved. So, major developments that is needed to commercialize this particular battery chemistry. And, what are the limitations that, we will talk one by one and their possible remedies.

So, overvoltage diffusion and solubility, then electrolyte in positive electrode which I mentioned in my last lecture. Porosity and amount of carbon that is important, surface area and of the carbon, carbon materials and the porosity, that is also important, along with the binder that is use the solvent, that is used in the electrolyte salts, that is used in inside the electrolyte.

Finally, operating conditions and performance. We will just introduce this concept and remaining two lectures, there will be case studies. We will take different materials and see how their performance is affected by slight modifications in them and what are the recent status. And finally, we will talk about the major players, who are doing research mostly in USA, one or two labs in Europe and Asia, particularly in Japan.

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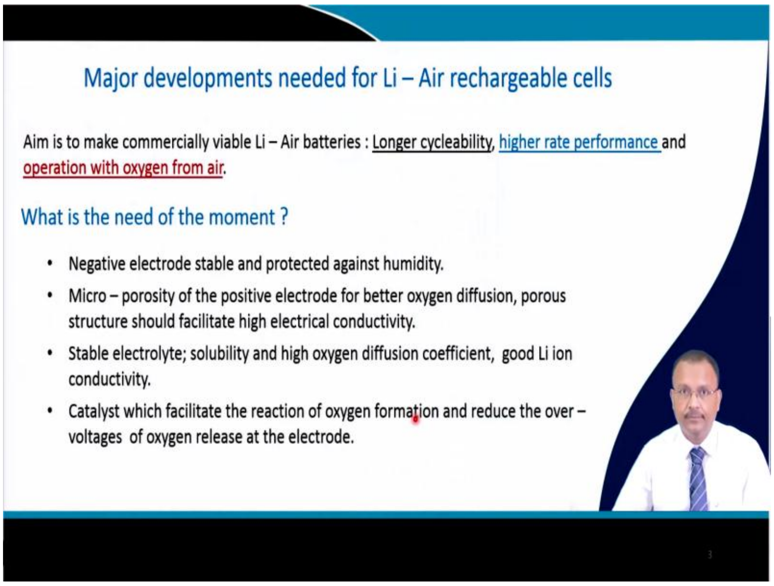

Major developments needed for Li – Air rechargeable cells

Aim is to make commercially viable Li – Air batteries : Longer cycleability, higher rate performance and operation with oxygen from air.

What is the need of the moment ?

- Negative electrode stable and protected against humidity.
- Micro – porosity of the positive electrode for better oxygen diffusion, porous structure should facilitate high electrical conductivity.
- Stable electrolyte; solubility and high oxygen diffusion coefficient, good Li ion conductivity.
- Catalyst which facilitate the reaction of oxygen formation and reduce the over – voltages of oxygen release at the electrode.

So, finally the aim is to make commercially viable lithium-air batteries, not lithium-oxygen batteries in R N D state. R N D whatever is being done, most of the cases Lithium-oxygen battery is being tried; but once you introduce air from open ambient, then you will have to face additional problems.

That battery should have longer cycleability. In most of the instances, cycleability is very poor; rate performance will have to improve, but in this till date the current is very low, discharge current is very low and as I said operation from oxygen from air. So, these are the three major requirements. So, the need of the moment is negative electrode should be stable and protected against humidity.

Number two is the micro-porosity of the positive electrode for better oxygen diffusion; porous structure is needed, but eventually they should have higher electrical conductivity as well. If it is too porous, that will not going to serve the purpose. Third is the stability of the electrode, electrolyte, solubility and high oxygen diffusion coefficients, and good Lithium-ion conductivity.

So, these are the prime requirement. And, catalyst which facilitate the reaction of oxygen formation and reduce the over voltage of oxygen release at the electrode. So, these four factors I have already described it, but these are the main four things that one should address.

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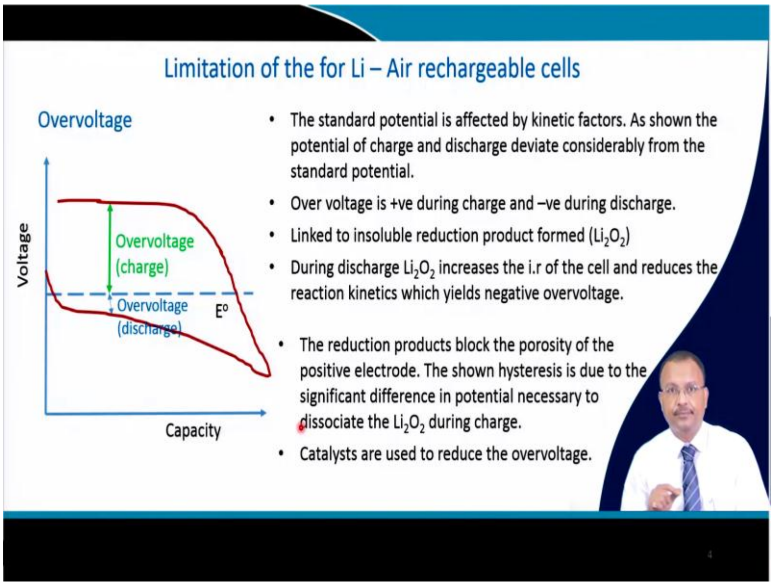

Limitation of the for Li – Air rechargeable cells

Overvoltage

- The standard potential is affected by kinetic factors. As shown the potential of charge and discharge deviate considerably from the standard potential.
- Over voltage is +ve during charge and –ve during discharge.
- Linked to insoluble reduction product formed (Li_2O_2)
- During discharge Li_2O_2 increases the i.r of the cell and reduces the reaction kinetics which yields negative overvoltage.
- The reduction products block the porosity of the positive electrode. The shown hysteresis is due to the significant difference in potential necessary to dissociate the Li_2O_2 during charge.
- Catalysts are used to reduce the overvoltage.

So, the standard potential of the battery which you can theoretically estimate, so that is affected by kinetic factor. So, this view graph you can see that, potential of charge and discharge, they considerably deviate from this value from the standard potential.

Over voltage this is positive that is during charge during charge operation, and it is smaller than the standard electrode potential. So, it is negative during discharge. So, there is link to insoluble reduction product from Li 2 O 2. So, somehow this over voltage is related to the formation of Li 2 O 2. So, during discharge the product is Li 2 O 2 that increases the internal resistance of the cell, and thereby they reduce the reaction kinetics, and which basically yields this negative over voltage.

The reduction product which is Li 2 O 2, that also block the porosity of the positive electrode. So, the hysteresis that is shown is basically due to the significant difference in potential necessary to dissociate Li 2 O 2 during charge. And, catalyst they are used basically to reduce the overvoltage. Some of the catalyst works well, but the process has not yet been fully optimized.

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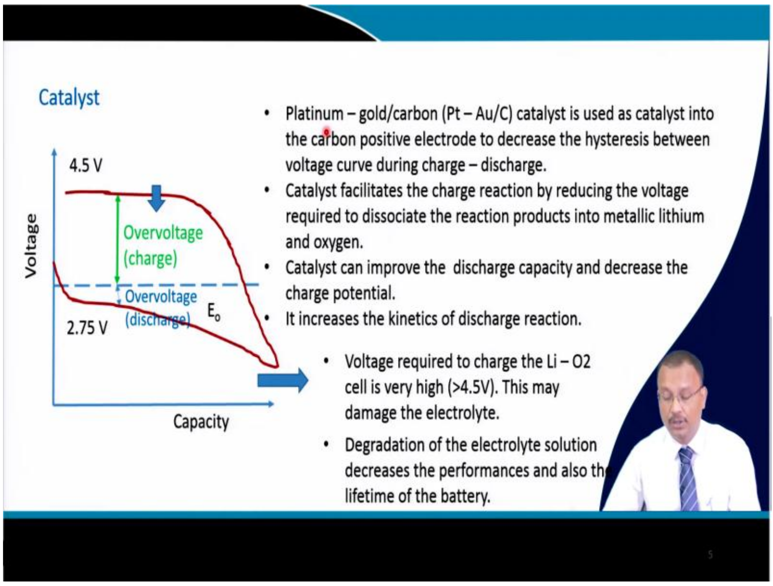

Catalyst

- Platinum – gold/carbon (Pt – Au/C) catalyst is used as catalyst into the carbon positive electrode to decrease the hysteresis between voltage curve during charge – discharge.
- Catalyst facilitates the charge reaction by reducing the voltage required to dissociate the reaction products into metallic lithium and oxygen.
- Catalyst can improve the discharge capacity and decrease the charge potential.
- It increases the kinetics of discharge reaction.
  - Voltage required to charge the Li – O2 cell is very high (>4.5V). This may damage the electrolyte.
  - Degradation of the electrolyte solution decreases the performances and also th lifetime of the battery.

So, one of such catalyst is expensive, Platinum-gold in carbon. So, this nano catalyst that is used with the carbon as positive electrode material, and that is basically to use the to reduce the hysteresis between this voltage curve, between the charge operation and the discharge part, so just to reduce it. And, this catalyst found to facilitates the charge reaction by reducing the voltage required to dissociate the reaction product into metallic Lithium and oxygen. So, catalysts play a major role in doing that.

This catalyst also can increase the discharge capacity and decrease the charge potential. So, eventually it increases the kinetics of the discharge reaction. So, the voltage required to charge this lithium oxygen cell is very high, usually 4.5 volt. This may damage the electrolyte. And, degradation of the electrolyte solution decrease the performance that you have seen in my last lecture; and thereby also the lifetime of the battery.

So, catalyst has a major role to play and all this Lithium-oxygen batteries therefore, use the catalyst. And the typical example I have shown this Platinum-gold that is used as catalyst material.

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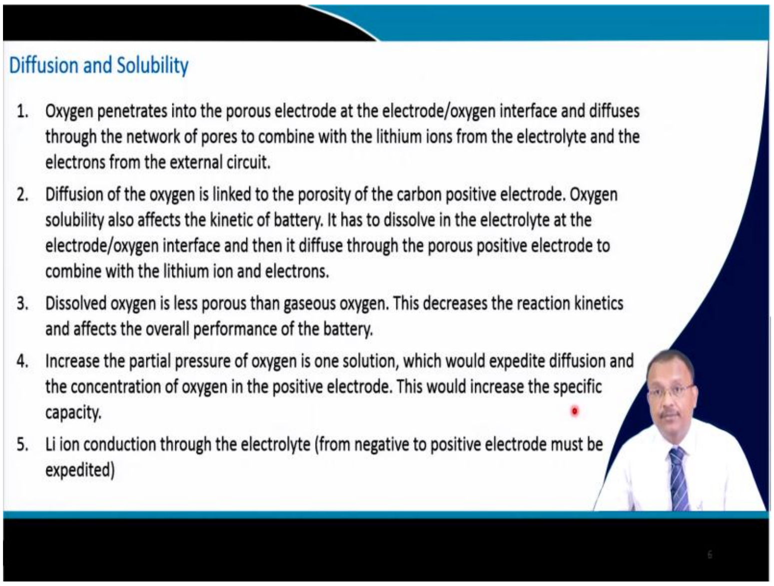

Diffusion and Solubility

1. Oxygen penetrates into the porous electrode at the electrode/oxygen interface and diffuses through the network of pores to combine with the lithium ions from the electrolyte and the electrons from the external circuit.
2. Diffusion of the oxygen is linked to the porosity of the carbon positive electrode. Oxygen solubility also affects the kinetic of battery. It has to dissolve in the electrolyte at the electrode/oxygen interface and then it diffuse through the porous positive electrode to combine with the lithium ion and electrons.
3. Dissolved oxygen is less porous than gaseous oxygen. This decreases the reaction kinetics and affects the overall performance of the battery.
4. Increase the partial pressure of oxygen is one solution, which would expedite diffusion and the concentration of oxygen in the positive electrode. This would increase the specific capacity.
5. Li ion conduction through the electrolyte (from negative to positive electrode must be expedited)

The second factor is diffusion and solubility. As you can understand now the oxygen penetrates into the porous electrode at the electrode oxygen interface and then they start to diffuse through the network of the pores to combine with the lithium ions from the electrolyte and the electron from the external circuit.

So, oxygen get reduced and then eventually it reacts with Li plus to form this peroxide. Sometimes, there is a intermediate product is involved, otherwise it directly froms Li 2 O 2. During charge, this Li 2 O 2 they dissociates to form Lithium and oxygen. So, diffusion of oxygen that is linked to the porosity of the carbon in the positive electrode, so that is quite straight forward.

The oxygen solubility also affects the kinetic of the battery. It has to dissolve in the electrolyte at the electrode oxygen interface and then to diffuse into the porous positive electrode to combine with the lithium ion and electron. So, it should have a good solubility in the electrolyte, in fact it will have to be dissolved in the electrolyte.

Now once it is dissolved, this oxygen is less porous than gaseous oxygen. So, actually in the diffuse oxygen their diffusion is limited, the rate of diffusion. So, it is not really less porous, it is diffusion is less than as compared to the gaseous oxygen. So, that eventually decreases you can understand, that will decrease the reaction kinetics and eventually affect the overall performance of the battery.

Increase of the partial pressure of the oxygen that is one solution, you can put lot of oxygen, you can force oxygen into the positive electrolyte in the positive electrode. And that will certainly expedite the diffusion and the concentration of oxygen in the positive electrode.

And this will certainly increase the specific capacity; because as you can see through the calculation that it will increase the specific capacity. Lithium-ion conduction through the electrolyte from negative to positive electrode, that also must be expedite. So, the solubility and the diffusion, these two parameters are important for you to get a reasonably good electrochemical performance.

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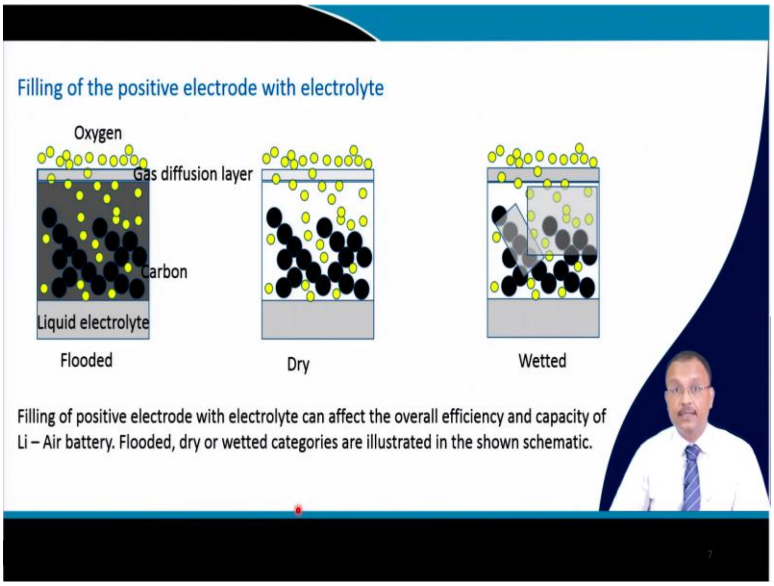

Filling of the positive electrode with electrolyte

Filling of positive electrode with electrolyte can affect the overall efficiency and capacity of Li – Air battery. Flooded, dry or wetted categories are illustrated in the shown schematic.

So, filling of the positive electrode with the electrolyte, there could be three possible case; the first one is as you can see it is flooded with the electrolyte. So, this is the porous carbon, and this is dissolved oxygen, and this is the gas diffusion layer. Carbons are these black balls, and this is the liquid electrolyte, and oxygen is coming from ambient through a oxygen permeable membrane.

So, the first one is flooded with electrolyte. The second configuration is something like that it is completely dry; so electrolyte is here, but it is not flooded with the electrolyte. And third one is partially wetted, part of it is wetted and part of is it is in dry.

So, this filling of the positive electrode with the electrolyte, that actually can affect the overall efficiency and capacity of the lithium-ion batteries. So, it is important whether it is dry, or it is wetted categories, and this let us examine it in little bit more details.

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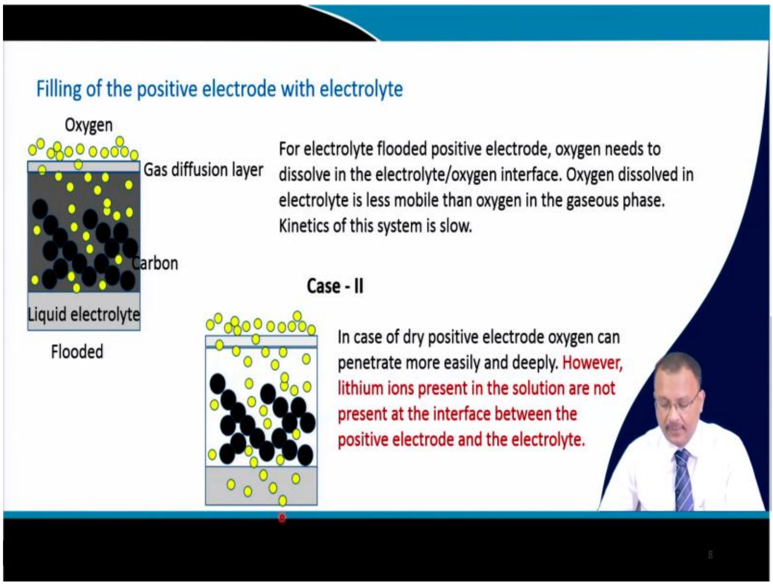

Filling of the positive electrode with electrolyte

For electrolyte flooded positive electrode, oxygen needs to dissolve in the electrolyte/oxygen interface. Oxygen dissolved in electrolyte is less mobile than oxygen in the gaseous phase. Kinetics of this system is slow.

Case - II

In case of dry positive electrode oxygen can penetrate more easily and deeply. However, lithium ions present in the solution are not present at the interface between the positive electrode and the electrolyte.

So, the first case is flooded one. So, the electrolyte flooded positive electrode, then oxygen needs to dissolve into the electrolyte oxygen interface. And, oxygen that is dissolved in electrolyte is less mobile that already I have mentioned. So, the diffusion coefficient is less than the oxygen that is in gaseous phase. So, eventually the kinetic of the system is slow.

Now the case II is totally dry. So, it is a dry positive electrode. So, oxygen can easily penetrate quite deep into the electrolyte solution. But the lithium-ion present in the solution, they are not present at the interface between the positive electrode and the electrolyte. So, this is one of the drawbacks of this system where it is completely dry.

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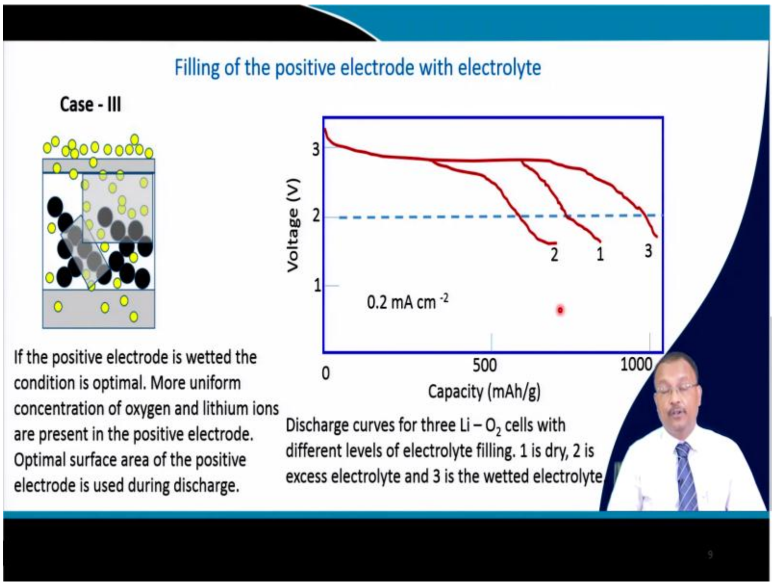

Filling of the positive electrode with electrolyte

Case - III

If the positive electrode is wetted the condition is optimal. More uniform concentration of oxygen and lithium ions are present in the positive electrode. Optimal surface area of the positive electrode is used during discharge.

Discharge curves for three Li – O_2 cells with different levels of electrolyte filling. 1 is dry, 2 is excess electrolyte and 3 is the wetted electrolyte

And the third case, this is wetting condition, partially wetted and this is considered to be more optimal, more uniform; because, here lithium is in close proximity. In the dry case lithium was up to this point and here with the electrolyte, you get lithium proximity.

And, oxygen ion diffusion also be relatively better; because this is not fully wetted, so partially wetted. So, more uniform concentration of oxygen and lithium ions are present in the positive electrode. And, optimal surface area of the positive electrode is used during discharge.

So, the surface area is important, because the porosity and surface area they are also interrelated. So, that is important for better oxygen diffusion inside the positive electrode. So, these are the three cases, where you can see that different types of different levels of electrolyte filling inside the positive electrode.

1 is dry, 2 is considered excess electrolyte. So, excess electrolyte is still not good; because of the poor oxygen ion diffusion, so that leads to the lowest capacity. And, number 3 is this wetted electrolyte, where close proximity of dissolved oxygen with lithium as well as better diffusion of oxygen into the positive electrode. So, that certainly increases the capacity. So, one can manipulate this after knowing this basic facts of filling of positive electrode with the electrolyte.

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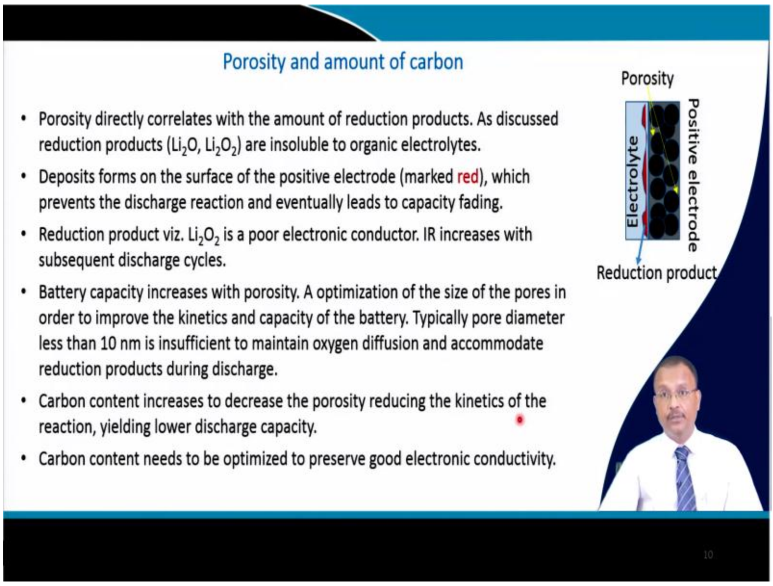

Porosity and amount of carbon

- Porosity directly correlates with the amount of reduction products. As discussed reduction products (Li_2O, Li_2O_2) are insoluble to organic electrolytes.
- Deposits forms on the surface of the positive electrode (marked red), which prevents the discharge reaction and eventually leads to capacity fading.
- Reduction product viz. Li_2O_2 is a poor electronic conductor. IR increases with subsequent discharge cycles.
- Battery capacity increases with porosity. A optimization of the size of the pores in order to improve the kinetics and capacity of the battery. Typically pore diameter less than 10 nm is insufficient to maintain oxygen diffusion and accommodate reduction products during discharge.
- Carbon content increases to decrease the porosity reducing the kinetics of the reaction, yielding lower discharge capacity.
- Carbon content needs to be optimized to preserve good electronic conductivity.

Now, porosity and amount of carbon, that is also important. And, why I am highlighting this is due to the fact that, when I will describe the case study; then you can correlate this factors with the actual experimental value that has been experimentally observed. So, for that you need to understand that why it is happening like that. So, here the porosity of the electrode and the total amount of carbon, so that also affect the electrochemical performance.

So, porosity directly correlates with the amount of the reduction product. So, reduction product is either intermediate Li 2 O or Li 2 O 2. And, they are insoluble in organic electrolyte. So, you can find this is actually on the surface of this. And if it is a porous mass, then it will go deep into it. I will show some example how it affects the electrochemical performance. So, this deposits form on the surface of the positive electrode, as you can see this is marked red.

So, this is the reduction product, and the blue colored thing is your electrolyte, black is your positive carbon and the porosity is marked here. So, this is the positive electrode. So, this prevents the discharge reaction and eventually leads to capacitive fading. So, due to the deposition of this Li 2 O 2 layer, so the porosity if it is there, then it can disperse inside the positive electrode material. So, the reduction product is a poor electronic conductor.

So, internal resistance of the battery increases with subsequent discharge cycle, because of their presence, and eventually that leads to the capacity fading. So, the battery capacity increases with porosity.

An optimization of the size of the pores is required in order to improve the kinetics and the capacity of the battery. Typical port diameter which is less than 10 nanometer, that is insufficient to maintain the oxygen diffusion and accommodate simultaneously the reduction product during discharge.

So, we will have to select, you will have to make this positive electrode in such a way, so that the porosity and amount of carbon. Of course, if the porosity is more, then the gas diffusion will be better; but at the same time the internal connectivity should also be maintained, because the electron should pass through this, right. So, if it is totally porous, so that is the problem. So, the carbon content increases to decrease the porosity that reduce the kinetics of the reaction yielding lower discharge capacity.

So, porosity is important. And carbon content needs to be optimized to preserve as I said good electronic conductivity. So, these factors you will have to keep it mind when you discharge the positive electrode, positive air electrode for lithium oxygen batteries.

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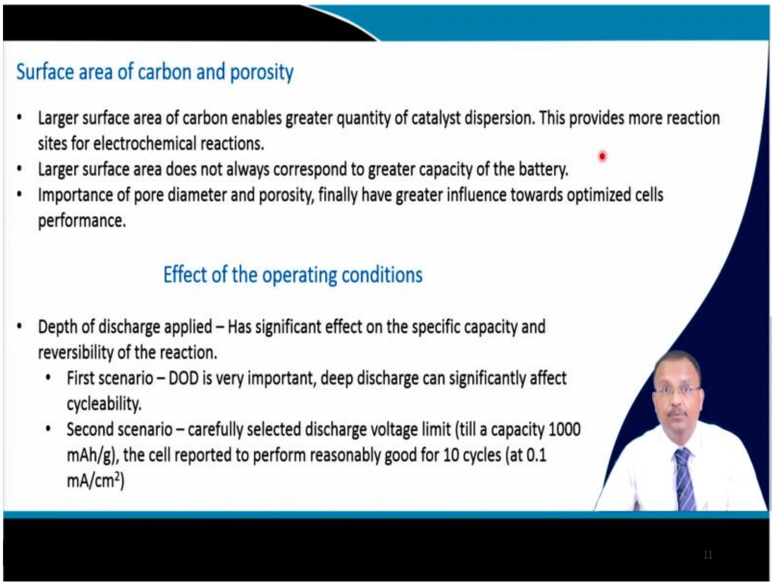

Surface area of carbon and porosity

- Larger surface area of carbon enables greater quantity of catalyst dispersion. This provides more reaction sites for electrochemical reactions.
- Larger surface area does not always correspond to greater capacity of the battery.
- Importance of pore diameter and porosity, finally have greater influence towards optimized cells performance.

Effect of the operating conditions

- Depth of discharge applied – Has significant effect on the specific capacity and reversibility of the reaction.
  - First scenario – DOD is very important, deep discharge can significantly affect cycleability.
  - Second scenario – carefully selected discharge voltage limit (till a capacity 1000 mAh/g), the cell reported to perform reasonably good for 10 cycles (at 0.1 mA/cm^2)

Surface area of carbon and porosity, they are also related. Large surface area of carbon, that actually enables a greater quantity of the catalyst. The catalyst is not shown in earlier slide; but you can consider manganese oxide or the platinum gold, whatever I mentioned that is also dispersed inside this in order to make a better oxygen reduction reaction (Refer Time: 20:05), so that helps and eventually that reduces the over voltage.

So, larger specific, larger surface area of the carbon that enables larger quantity of the catalyst dispersion and that eventually provides more reaction sites for the electrochemical reactions. And larger surface area does not always correspond to greater capacity of the battery. Importance of the pore diameter and the porosity, finally have greater influence towards the optimized cell performance.

Because, we will have to always see that porosity should be there; but interconnection is also to be maintained, so that electron transfer is not get impeded. So, I will cite some examples which will correlate with this factors that, operating condition that is also that also affects the electrochemical performance.

The first and foremost is the depth of discharge. You cannot on I mean you can discharge the battery; but the depth of discharge is very important, it has significant effect on the specific capacity and the reversibility of the reaction. So, if I consider the first scenario, where DOD is important and deep discharge that can significantly affect the cycleability.

So, cycleability will be dramatically fall, if you deep discharge the material, right. Because, when you charge it back, then you will have to dissociate this reaction product Li 2 O 2. So, sometimes it is not very easy from that low voltage to go to higher voltage to dissociate the lithium and oxygen.

Second scenario is if you carefully select the discharge voltage and eventually as you can understand if the discharge voltage is kept little bit up, then your capacity will be affected little bit. So, capacity say about 1000, you have selected a particular DOD; then one can find that this lithium oxygen cell performs reasonably well.

Reasonably well means only 10 cycles at a very low current rate, still it is not optimized; but people have found that the so-called DOD, they have a major role to play in deciding the electrochemical performance.

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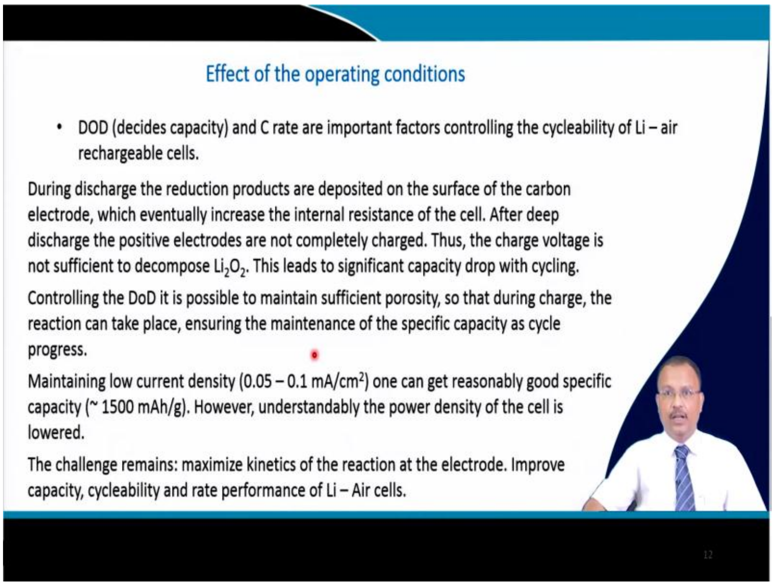

Effect of the operating conditions

- DOD (decides capacity) and C rate are important factors controlling the cycleability of Li – air rechargeable cells.

During discharge the reduction products are deposited on the surface of the carbon electrode, which eventually increase the internal resistance of the cell. After deep discharge the positive electrodes are not completely charged. Thus, the charge voltage is not sufficient to decompose Li_2O_2. This leads to significant capacity drop with cycling.

Controlling the DoD it is possible to maintain sufficient porosity, so that during charge, the reaction can take place, ensuring the maintenance of the specific capacity as cycle progress.

Maintaining low current density (0.05 – 0.1 mA/cm^2) one can get reasonably good specific capacity (~ 1500 mAh/g). However, understandably the power density of the cell is lowered.

The challenge remains: maximize kinetics of the reaction at the electrode. Improve capacity, cycleability and rate performance of Li – Air cells.

So, the DOD that decides the capacity and the C rate is also important that factor control the cycleability of lithium air rechargeable cell. So, at very high current discharge rate, your capacity fades very fast. So, you can understand that why it is happening so. During discharge the reduction products that are deposited on the surface, you know that this red thing what I showed in one of the schematics.

So, they are basically deposited on the surface of the carbon electrode and that eventually increase the internal resistance of the cell. And when you do the deep discharge, the positive electrodes are not completely charged. So, the charge voltage is not sufficient to decompose this Li 2 O 2, because you will have to go to a large charge voltage. So, that is that may not be sufficient to decompose the whole Li 2 O 2, which formed as a discharge product, and this leads to significant capacity drop with subsequent cycling.

So, the controlling of this depth of discharge if it is possible; then you can in order to do that, you will have to maintain sufficient porosity, so that during charge reaction during the charge the reaction then take place and ensuring the maintenance of the high specific capacity of the cycling progress. So, you have supplied enough voltage for this reaction product to get dissociated.

Maintaining the low current density, that is important about 0.05 to 0.1 milli ampere per centimeter square. One can usually get reasonable good specific capacity about 1500 milliampere hour per gram, which is quite large as compared to normal lithium ion battery which is something around 170 to 190 milliampere hour per gram. So, almost three times increase; but understandably the power density will be low, because you cannot drain much current out of this cell.

So, the challenge remains, maximize the kinetics of the reaction at the electrode, improve the capacity, improve the cycleability and rate performance for this battery. Still, it is an open field and research should go on for this particular areas.

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Major players in Li – Air battery

1. **Yardney Technical Products Inc. /Lithion** (Pawcatuck, Connecticut) [https://www.ctihub.com/show/yardney-technical-products-inc] – 256 cm^2 prototype designed. Added adjuvant to increase the oxygen diffusion coefficients. At 0.05 mA/cm^2 capacity was 2500 mAh/g whereas at 2 mA/cm^2, capacity drops down to 200 mAh/g. (Not sure if the company exists today)
2. **PolyPlus Battery Company (Berkeley, California)** [https://polyplus.com] – Interesting work on aqueous electrolyte with the integration of a protective layer of ceramic LISICON on the surface of the lithium anode.
3. **LiOX Power** – A startup company in Pasadena, California (www.liox.com) (No further information available in their website).
4. **Excellatron Solid State LLC** – Develop lithium – air batteries for applications in cellphones, airplanes and the space industry. [www.excellatron.com]
5. **IBM (Almaden Lab in San Jose, California)** [www.research.ibm.com/labs/almaden]

Now, major players if you see in lithium-ion battery; the first one this Yardney Technical Products, they are all small companies, US based company in Connecticut. I tried to access their website, first they prepared 256-centimeter square prototype they designed.

So, they added some kind of additive, I do not know that what kind of additive was added to increase oxygen diffusion coefficient. The report is at 0.05 milliampere per centimeter square. This current rate, the capacity was reasonably high 2500 milliampere hour per gram. If you increase the current to 2 milliampere per centimeter square, this capacity drops to dramatically 200 milliampere hour per gram.

I tried to access their website, but I not sure that whether the company exists today. They were working in this field. This PolyPlus Battery, it is also in California; you can access their website, so they are doing some interesting work. And have some information about their research and you can access and see exactly; what they are doing, they are using aqueous electrolyte with the integration of a protective layer of ceramic LISICON.

You know about NASICON, sodium ion super ionic conductor; it is lithium-ion super ionic conductor that is used at the surface of the lithium anode to protect. And I think that this company is still they are doing some aggressive research. LiOX Power, this is this was a startup company in again in California.

So, try to access their website, but no information I could gather. And either they are still doing the research; they say that you can send them the email and they will reply back, no further information was given what exactly they are doing. This Excellatron Solid State LLC, they develop lithium air batteries for the application in small cell phone and some aeroplane related applications and application in the space battery.

So, you can access their website, but the chemistry is very simple straight forward; but what they are doing in terms of the electrolyte, what kind of solvent they are using, what kind of salt they are using, what kind of porosity in the carbonaceous material, what type of carbonaceous material they are using. What type of catalyst they are using, this kind of details usually that is difficult to get, unless you start reading the research papers.

IBM Lab in San Jose, California, this is also a good source. So, this website is also accessible to see exactly what they are doing. This is important technology and people should be knowledgeable enough to attack the existing problem, to get a good quality battery which is easy to recycle, and which will have a very high energy density, because air is in one end and lithium metal both are light weight. So, this is in my consideration this is very good technology to pursue further.

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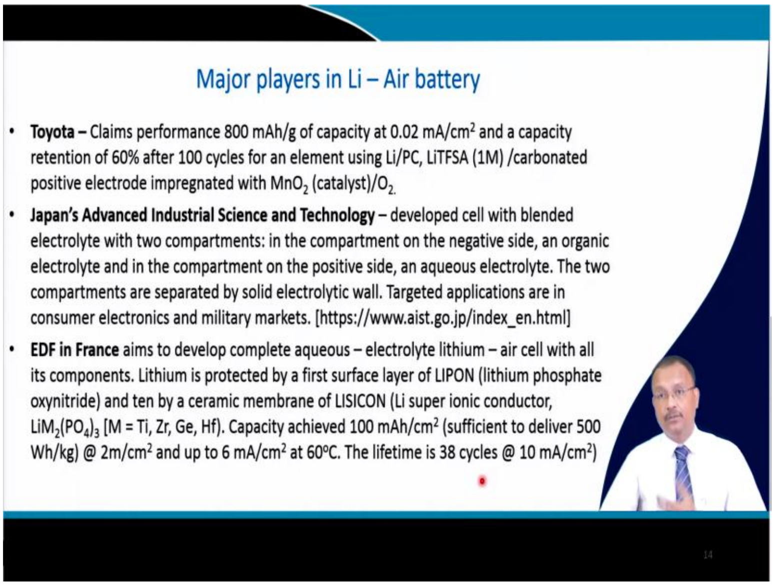

Major players in Li – Air battery

- **Toyota –** Claims performance 800 mAh/g of capacity at 0.02 mA/cm^2 and a capacity retention of 60% after 100 cycles for an element using Li/PC, LiTFSA (1M) /carbonated positive electrode impregnated with MnO_2 (catalyst)/O_2.
- **Japan's Advanced Industrial Science and Technology –** developed cell with blended electrolyte with two compartments: in the compartment on the negative side, an organic electrolyte and in the compartment on the positive side, an aqueous electrolyte. The two compartments are separated by solid electrolytic wall. Targeted applications are in consumer electronics and military markets. [https://www.aist.go.jp/index_en.html]
- **EDF in France** aims to develop complete aqueous – electrolyte lithium – air cell with all its components. Lithium is protected by a first surface layer of LIPON (lithium phosphate oxynitride) and ten by a ceramic membrane of LISICON (Li super ionic conductor, $LiM_2(PO_4)_3$ [M = Ti, Zr, Ge, Hf). Capacity achieved 100 mAh/cm^2 (sufficient to deliver 500 Wh/kg) @ 2m/cm^2 and up to 6 mA/cm^2 at 60°C. The lifetime is 38 cycles @ 10 mA/cm^2)

In Asia the Toyota, they are working on it. So, they claims to perform this 800 milliampere hour per gram capacity at that low current. And capacity retention about 60 percent in 100 cycles. So, they use lithium and polycarbonate, then LiTFSA 1 molar in carbonated positive electrode impregnated with MnO 2 s catalyst, and air is coming from, sorry oxygen is coming from pure oxygen. So, they have not tried yet the air battery.

So, Toyota is working means, as you understand their purpose is for E V. So, is futuristic technology, so spending lot of money on it. Japan's Advanced Industrial Science and Technology, they develop cell with blended electrolyte, that I mentioned the fourth one in my category with two compartments.

The compartment of negative side as you understand organic electrolyte, and compartment in the positive side aqueous electrolyte; the two compartment are separated by a solid electrolyte; value, may not access exactly what type of solvent, salt, solid electrolyte they are using, because that is all patented technology.

And their targeted applications are again in consumer electronics, that tells me that they are targeting low current density battery and particularly for military market. So, E V is a long way to go, but consumer electronics probably they are working on to use in their E V for a smaller power requirement, and you can access, sorry I was talking about Toyota.

So, this is also they support industries, but you can go to this site to see exactly what they are doing. EDF in France, they aim to develop a complete aqueous electrolyte lithium air cell with its component. Lithium is protected, the first surface layer is the lithium conducting, lithium phosphate oxynitrate which we call LIPON and then by there is a spelling mistake, then by a ceramic membrane called LISICON, lithium super ionic conductor which is same like NVP kind of material. Instead of NVP, this is lithium and one metal it could be titanium, zirconium, germanium or hafnium.

And phosphate-based poly anion, you know about this structure. The capacity achieved is 100 milliampere per hour per centimeter square. So, that is sufficient to deliver about 500 watt hour per kg at 2 milliampere, this is 2 milliampere per centimeter square, A is missing here and up to 6 milliampere per centimeter square, 60 degree Celsius. The lifetime as you can see lot of chances to improve it, only 38 cycles and that is at 10 milliampere hour per centimeter square.

We will come back to this, and we will see the case study that what kind of lithium, metal, what kind of carbonaceous material, what kind of catalyst people are using, what kind of porosity with exact experimental data in my last two lectures in this module.

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REFERENCES

- **Christian Glaize and Sylvie Genies** "Lithium batteries and other electrochemical storage systems, Chapter – 10 page 297 – 306 and all references (Study material)
- **P K Shen et. al (Eds)** "Electrochemical Energy Advanced Materials and Technologies", Chapter – 8 Advanced Materials for Li – Air Rechargeable Batteries (Study material)

So, the books remain same, only the page numbers its highlighted where you will this will act as your study material.

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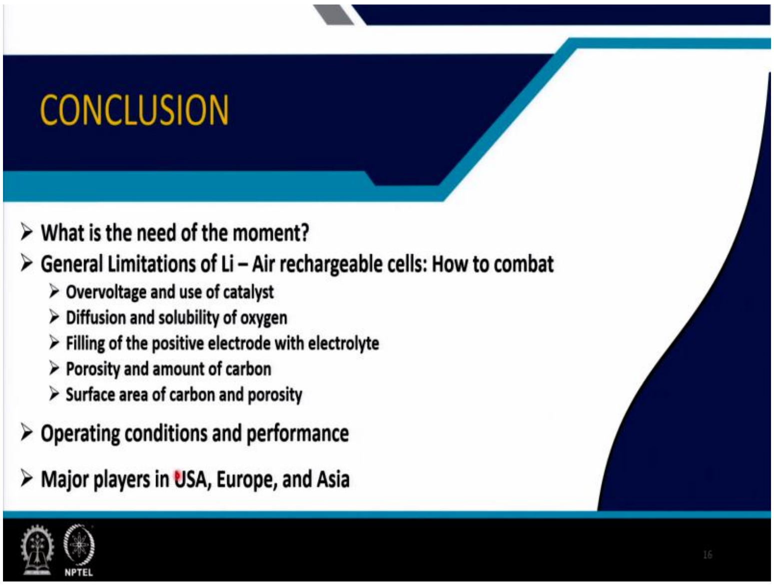

CONCLUSION

- What is the need of the moment?
- General Limitations of Li – Air rechargeable cells: How to combat
    - Overvoltage and use of catalyst
    - Diffusion and solubility of oxygen
    - Filling of the positive electrode with electrolyte
    - Porosity and amount of carbon
    - Surface area of carbon and porosity
- Operating conditions and performance
- Major players in USA, Europe, and Asia

And here in this lecture, first we talked about what is the need of the moment, then general limitations and how to solve lithium air rechargeable batteries, how to combat their problems.

We talked about overvoltage and use of catalyst to nullify this over voltage, then diffusion and solubility of oxygen, what are their importances and filling the positive electrode with electrolyte. So, three different types of cases were identified with the partial wettability, positive electrode that provides a better electrochemical performance.

Then porosity and amount of carbon that one should use, then surface area and of the carbon and the porosity, they are interrelated and how much one should use for better performance.

Then operating conditions and performance they are related. We talked about the depth of discharge, effect of depth of discharge and porosity in maintaining the capacity. And finally, a few list of companies which are coming up; they are major players in mostly USA and Asia, particularly in Japan, that was highlighted.

Thank you for your attention.