# Electrochemical Energy Storage

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## Module - 11
## Li - Air Batteries
## Lecture - 41
## Operational Principles of Aqueous and Li - O 2 Batteries

Welcome to my course Electrochemical Energy Storage and this is module number 11 where I will introduce the new concept on lithium-ion batteries and this is known as Lithium-Air Batteries. And this is lecture number 41 where we will be talking about the Operational Principles of Aqueous as well as organic electrolyte based Lithium oxygen Batteries.

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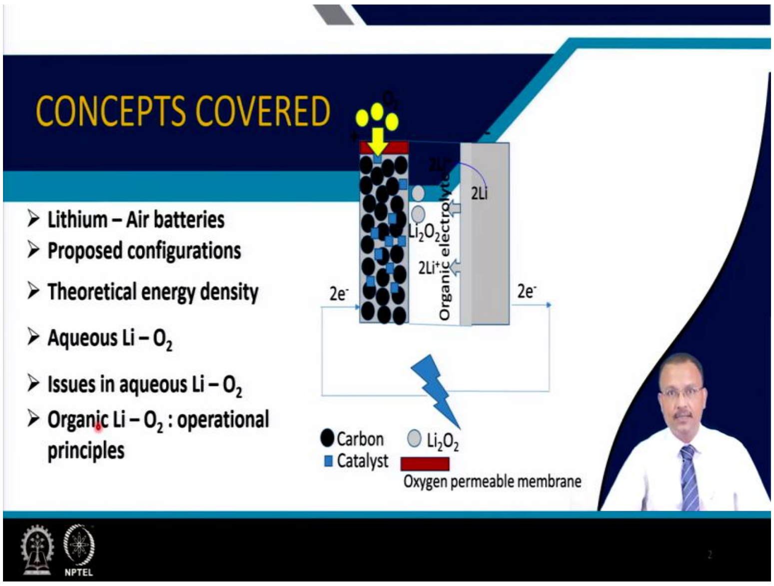

CONCEPTS COVERED

- Lithium – Air batteries
- Proposed configurations
- Theoretical energy density
- Aqueous Li – $O_2$
- Issues in aqueous Li – $O_2$
- Organic Li – $O_2$ : operational principles

Now, this is a new concept this has not yet been commercialized, although many of the companies they are working on it and very simple configuration, lithium in one side and simple air in the other side. So, this we will discuss in details.

So, what are the proposed configurations of these batteries and then we would like to know about the theoretical energy density of these batteries and you will find it is far superior than existing lithium-ion batteries. So, that is the motivation of working in this particular configuration.

Then, we will talk about aqueous electrolyte based lithium-air or lithium oxygen batteries, then what are the issues that is involved and then finally, replacing this aqueous electrolyte with organic electrolyte and what are the operational principles. So, this will discuss in details.

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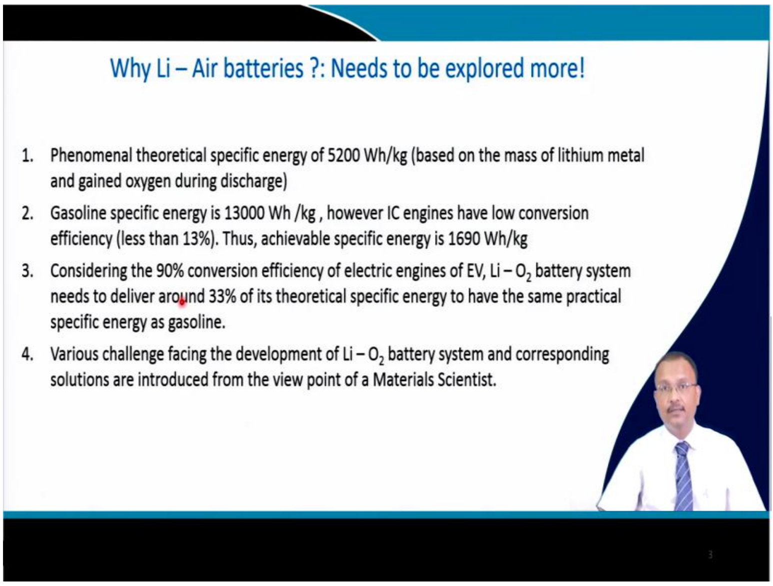

Why Li – Air batteries ?: Needs to be explored more!

1. Phenomenal theoretical specific energy of 5200 Wh/kg (based on the mass of lithium metal and gained oxygen during discharge)
2. Gasoline specific energy is 13000 Wh /kg , however IC engines have low conversion efficiency (less than 13%). Thus, achievable specific energy is 1690 Wh/kg
3. Considering the 90% conversion efficiency of electric engines of EV, Li – $O_2$ battery system needs to deliver around 33% of its theoretical specific energy to have the same practical specific energy as gasoline.
4. Various challenge facing the development of Li – $O_2$ battery system and corresponding solutions are introduced from the view point of a Materials Scientist.

Now, the first question is that why should I go for this technology? So, the first cause is phenomenal theoretical specific energy as high as 5200 watt hour per kg and that is only once I calculate the specific capacity based on the mass of lithium metal and the oxygen that it gains during discharge. Now, if you consider the gasoline specific energy it is 13000 watt hour per kg. But as you know IC engine they have low conversion efficiency almost less than 13 percent.

So, the achievable specific energy is about 1690 watt hour per kg. So, if you consider that unlike this IC engine about 90 percent conversion efficiency of electric engine of electric vehicles. Then lithium oxygen battery system they needs to deliver about 33 percent of its theoretical specific energy that is to match the practical specific energy of gasoline which is doable.

So, that is why people are so much interested to go for lithium-air batteries. But there are various challenges for the development of this lithium-oxygen battery system. And, we will look at the solution that we can think of because it is not yet commercialized. So, the solution that we can think of purely from a material science personnel that point of view, so, that is the motive.

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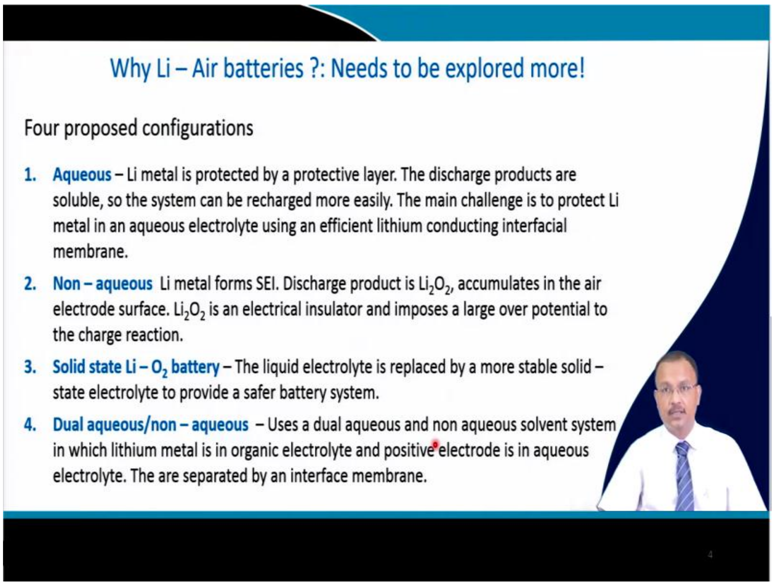

## Why Li – Air batteries ?: Needs to be explored more!

Four proposed configurations

1. **Aqueous** – Li metal is protected by a protective layer. The discharge products are soluble, so the system can be recharged more easily. The main challenge is to protect Li metal in an aqueous electrolyte using an efficient lithium conducting interfacial membrane.
2. **Non – aqueous** Li metal forms SEI. Discharge product is $Li_2O_2$, accumulates in the air electrode surface. $Li_2O_2$ is an electrical insulator and imposes a large over potential to the charge reaction.
3. **Solid state Li – $O_2$ battery** – The liquid electrolyte is replaced by a more stable solid – state electrolyte to provide a safer battery system.
4. **Dual aqueous/non – aqueous** – Uses a dual aqueous and non aqueous solvent system in which lithium metal is in organic electrolyte and positive electrode is in aqueous electrolyte. The are separated by an interface membrane.

So, briefly four kinds of configuration has been proposed. The first one is quite interesting aqueous electrolyte is used. So, lithium metal you know that it will have to be protected because you cannot use aqueous based electrolyte. So, lithium metal is protected by a protective layer, so that it does not come into direct contact with the electrolyte.

Now, the discharge products they are soluble, soluble in the electrolyte. So, eventually that will aid to the easy recharge of this battery system. So, the main challenge remains to protect the lithium metal in aqueous electrolyte using efficient lithium conducting interfacial membrane, right because lithium ion should be able to pass, but as a whole this lithium metal anode should not react with the electrolyte.

So, that is the 1st system. 2nd one is non-aqueous. So, in case of non-aqueous electrolyte usually organic base electrolyte is used and you by this time you know that lithium metal during the forming cycle they form this solid electrolyte interface. Usually the discharge product is $Li_2O_2$ superoxide of lithium and that accumulates in the air electrode surface because it is not a pure air electrode as you will be see seen that we use porous carbon as the positive electrode material where from oxygen can diffuse through.

But, this discharge product lithium oxygen this is basically electrical insulator. So, if since it is electrical insulator, it will impose a large over potential to the charge reaction. So, during the charge reaction it will cause the over potential. So, that is one of the problems for this batteries. It is non-aqueous electrolyte based lithium-air batteries.

3rd one is solid state lithium oxygen battery here the liquid electrolyte is completely replaced by a stable solid state electrolyte to provide a safer battery system and 4th one is a dual aqueous as well as non-aqueous this kind of battery.

So, it as the name suggests, it uses a dual aqueous and non-aqueous solvent system in which lithium metal is an organic electrolyte. So, there is no chance of getting it reacted with the electrolyte and positive electrode is in aqueous electrolyte. And, of course, they are separated by an interface membrane.

So, these are the four configurations and research work is being pursued for all these four individual lithium-oxygen system.

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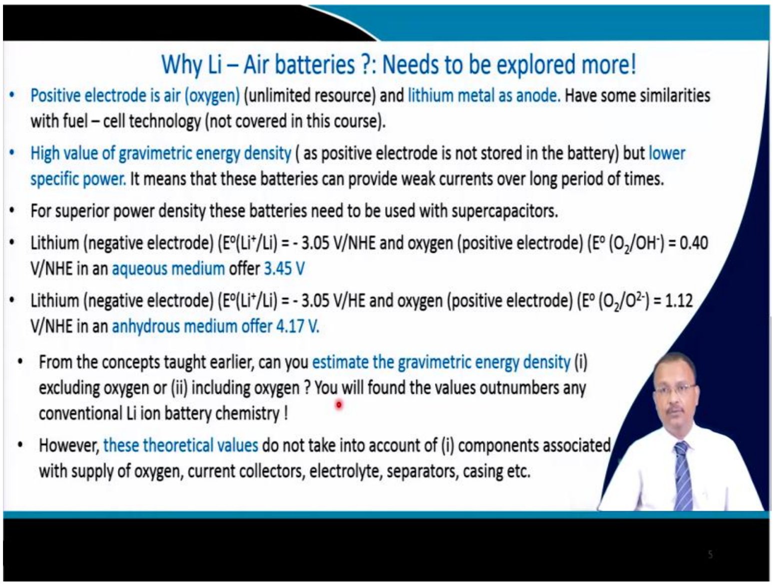

Why Li – Air batteries ?: Needs to be explored more!

- Positive electrode is air (oxygen) (unlimited resource) and lithium metal as anode. Have some similarities with fuel – cell technology (not covered in this course).
- High value of gravimetric energy density ( as positive electrode is not stored in the battery) but lower specific power. It means that these batteries can provide weak currents over long period of times.
- For superior power density these batteries need to be used with supercapacitors.
- Lithium (negative electrode) ($E^o(Li^+/Li)$ = - 3.05 V/NHE and oxygen (positive electrode) ($E^o$ ($O_2/OH^-$) = 0.40 V/NHE in an aqueous medium offer 3.45 V
- Lithium (negative electrode) ($E^o(Li^+/Li)$ = - 3.05 V/HE and oxygen (positive electrode) ($E^o$ ($O_2/O^{2-}$) = 1.12 V/NHE in an anhydrous medium offer 4.17 V.
- From the concepts taught earlier, can you estimate the gravimetric energy density (i) excluding oxygen or (ii) including oxygen ? You will found the values outnumbers any conventional Li ion battery chemistry !
- However, these theoretical values do not take into account of (i) components associated with supply of oxygen, current collectors, electrolyte, separators, casing etc.

Now, as I have said here the positive electrode is air. So, air contains about 20 percent of oxygen and it is considered to be unlimited resource. So, we do not have to think about air I mean oxygen in air, and lithium metal as anode and in the subsequent lecture we will be talking about the lithium recycling. So, recycling is a bit easier here.

So, directly you are using lithium metal. You do not have the problem to extract lithium from the already formed ceramic oxide various types of ceramic oxides or phosphate based system. So, lithium can be easily extracted. So, in that way there are some similarities with fuel cell technology where hydrogen reacts with oxygen. Of course, this is not covered in this particular course, but some similarity one can find out.

So, it is having a high value of gravimetric energy density as the positive electrode is not stored in the battery. So, oxygen is coming from outside, but it usually is having lower specific power. You cannot drain lot of current because of the kinetic limitations for this kind of reactions. So, that only means that these batteries can provide weak currents over long period of time. So, consumer electronics application this is quite useful.

For superior power density these batteries needed to be used with super capacitor. In one of my lectures we talked about bat cap battery capacitor hybrid. So, something similar can be made with this system as well. So, that is one advantage and lithium that is negative electrode. So, if you have a standard electrode potential it is about minus 3.05 volt versus normal hydrogen electrode.

And, oxygen that is positive electrode. So, in aqueous system this standard energy standard reduction potential is about 0.40. So, in aqueous medium it offers about 3.45 volt theoretically. Now, again lithium negative electrode it gives minus 3.05 volt and oxygen in positive electrode in anhydrous medium that gives about 1.12 volt. So, in anhydrous medium theoretically it should offer 4.17 volt.

Now, from the concept that I taught you earlier you should theoretically estimate the gravimetric energy density. So, first you will have to consider that oxygen is not included; that means, oxygen is coming from the ambient, constant flow is maintained, you are not carrying a oxygen cylinder. So, what will be the gravimetric energy density? And, second is including oxygen.

So, once you calculate it you will find that these values outnumbers any conventional lithium-ion battery chemistry. So, that is why it is so important, but this theoretical values, they do not take into account of the other components which is associated with oxygen supply, use of current collector, use of electrolyte, separator, casing etcetera. So, gravimetric energy density it will be lowered as compared to the theoretical energy density what you will calculate.

So, initially I thought that I will ask you to calculate it, but I will give you some hints and you can work it on.

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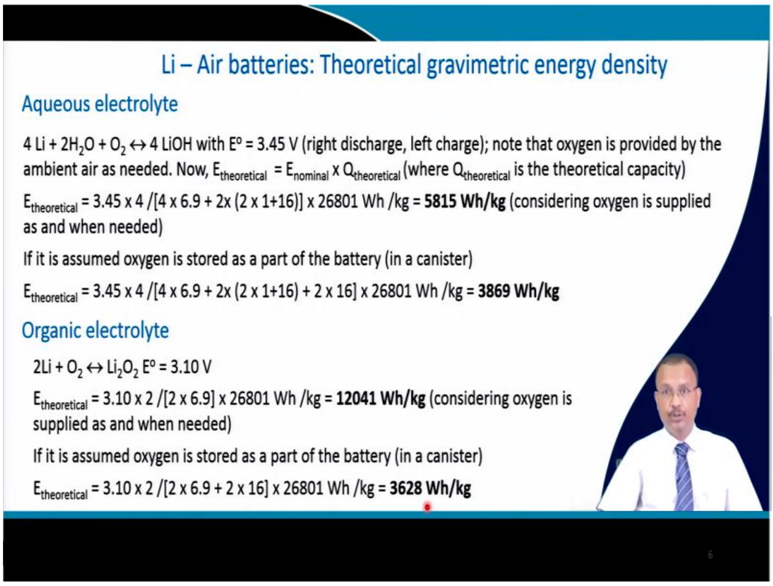

## Li – Air batteries: Theoretical gravimetric energy density

### Aqueous electrolyte

$4\,Li + 2H_2O + O_2 \leftrightarrow 4\,LiOH$ with $E^o = 3.45$ V (right discharge, left charge); note that oxygen is provided by the ambient air as needed. Now, $E_{theoretical} = E_{nominal} \times Q_{theoretical}$ (where $Q_{theoretical}$ is the theoretical capacity)

$E_{theoretical} = 3.45 \times 4 / [4 \times 6.9 + 2\times (2 \times 1+16)] \times 26801$ Wh /kg = **5815 Wh/kg** (considering oxygen is supplied as and when needed)

If it is assumed oxygen is stored as a part of the battery (in a canister)

$E_{theoretical} = 3.45 \times 4 / [4 \times 6.9 + 2\times (2 \times 1+16) + 2 \times 16] \times 26801$ Wh /kg = **3869 Wh/kg**

### Organic electrolyte

$2Li + O_2 \leftrightarrow Li_2O_2$ $E^o = 3.10$ V

$E_{theoretical} = 3.10 \times 2 / [2 \times 6.9] \times 26801$ Wh /kg = **12041 Wh/kg** (considering oxygen is supplied as and when needed)

If it is assumed oxygen is stored as a part of the battery (in a canister)

$E_{theoretical} = 3.10 \times 2 / [2 \times 6.9 + 2 \times 16] \times 26801$ Wh /kg = **3628 Wh/kg**

And see whether whatever I have deduced whether it makes sense. So, first consider aqueous electrolyte. So, in aqueous electrolyte the reaction is something like this – lithium is reacting with dissolved oxygen and H 2 O to form lithium hydroxide. So, the value of standard electrode potential is 3.45 volt; the right reaction is discharged. So, first the discharge will take place and the left reaction it will dissociate to get back the lithium.

$4\ Li + 2H_2O + O_2 \leftrightarrow 4\ LiOH$ with $E^o = 3.45$ V

So, it is to be noted that oxygen is provided by the ambient air as needed, right. So, you do not have any oxygen canister oxygen cylinder carrying with the batteries. So, you know that this theoretical energy is the nominal voltage into the capacity. So, Q theoretical is the theoretical capacity. Now, theoretical capacity will be able to calculate based on the Faraday's equation. I hope that you remember it n by m into this number 26801.

So, here is the nominal voltage and 4 electrons are involved. So, this 4 divided by the molecular weight and I am not considering this oxygen because assuming it is coming from the air. So, only the water mass is included along with the lithium and you multiply it 26801 you get a big number 5815 watt hour per kg. So, as I said oxygen is supplied as and when needed from the air. So, that is one way to estimate it and a huge energy density you will get.

$E_{theoretical}$ = 3.45 x 4 /[4 x 6.9 + 2x (2 x 1+16)] x 26801 Wh /kg = **5815 Wh/kg**

Now, if you assume that the oxygen is stored then you will have to take into account this weight. So, remaining everything will remain same 3.45 into 4 divided by 4 into 6.94 lithium 2 into twice H 2 O plus 2 into molecular oxygen into 26801 that constant number. So, that will give you a slightly lower value 3869 watt hour per kg.

$E_{theoretical}$ = 3.45 x 4 /[4 x 6.9 + 2x (2 x 1+16) + 2 x 16] x 26801 Wh /kg = **3869 Wh/kg**

Now, if you replace it with organic electrolyte this product is not dissolved into the electrolyte. So, it get separated on the positive electrode surface so that is one of the problems because it is having very poor electronic conductivity. Now, the standard electrode potential is assumed 3.10 volt. So, 3.10 volt if you take and 2 electron transfer is happening and oxygen is supplied as and when needed.

$2Li + O_2 \leftrightarrow Li_2O_2$ $E^o = 3.10$ V

$E_{theoretical}$ = 3.10 x 2 /[2 x 6.9] x 26801 Wh /kg = **12041 Wh/kg** (considering oxygen is supplied as and when needed)

So, I am not taking into account the oxygen weight multiply by this number you get a huge number 12041 watt hour per kg. And, remember that this is not the exact value because you will have to put the weight of the other components that you are using in the cell like other lithium ion cell as well.

But, this is just to give you an idea that as compared to the normal lithium ion battery which is typically 250 to 300 watt hour per kg you are getting enormously high number. Even if you consider those weight no way the existing lithium ion battery technology they can match this kind of energy density.

Now, if you assume the oxygen is stored as a part of the battery then this oxygen weight will come into picture then also you will get 3628 almost 10 times increase of the existing theoretical energy density of the battery chemistry that we use commercially today. So, we have fairly good advantage to use this.

If it is assumed oxygen is stored as a part of the battery (in a canister)

$E_{theoretical} = 3.10 \times 2 / [2 \times 6.9 + 2 \times 16] \times 26801$ Wh /kg = **3628 Wh/kg**

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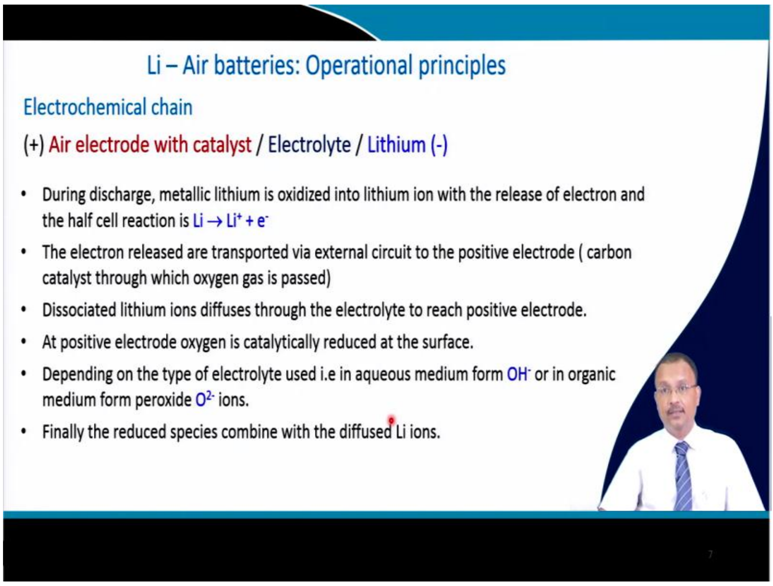

### Li – Air batteries: Operational principles

Electrochemical chain

(+) Air electrode with catalyst / Electrolyte / Lithium (-)

- During discharge, metallic lithium is oxidized into lithium ion with the release of electron and the half cell reaction is $Li \rightarrow Li^+ + e^-$
- The electron released are transported via external circuit to the positive electrode ( carbon catalyst through which oxygen gas is passed)
- Dissociated lithium ions diffuses through the electrolyte to reach positive electrode.
- At positive electrode oxygen is catalytically reduced at the surface.
- Depending on the type of electrolyte used i.e in aqueous medium form $OH^-$ or in organic medium form peroxide $O^{2-}$ ions.
- Finally the reduced species combine with the diffused Li ions.

Now, the electrochemical cell, if you consider positive electrode is usually air electrode something where from the air can pass,I am assuming the oxygen is reacting with lithium. So, but still sometimes we call it lithium-oxygen battery sometimes we call it lithium-air batteries.

So, some catalyst is needed I will explain what is the role of the catalyst in the positive electrode, then you have electrolyte and then you have lithium as negative electrode. So, first the discharge reaction takes place metallic lithium is oxidized to lithium ion and electron is released in the sub cell reaction. So, you can consider this a half cell because you are measuring the voltage with respect to the lithium and lithium is acting as the negative electrode.

Now, the electron released are transported by external circuit because we will get power out of this reaction. So, first the discharge reaction will take place and it comes to the positive electrode. And usually the positive electrode is carbon porous carbon is used and some catalyst is there along with the porous carbon and oxygen gas is passed through this positive electrode. Remember the first schematic that I had showed in the first slide.

Then dissociated lithium ion diffuses through the electrolyte to reach the positive electrode. This dissociated lithium ion through the electrolyte it moves and reach the positive electrode. Now, in the positive electrode oxygen is catalytically reduced at the surface. So, it gets the electron and it gets reduced and catalyst helps this oxygen reduction reaction ORR.

Depending on the type of the electrolyte used that is whether you are using aqueous medium then it forms hydroxyl ion or if you are using an inorganic medium, it forms a peroxide ions. So, it depends on the electrolyte whatever you are using and you remember that initially either it forms lithium hydroxide in case of aqueous electrolyte or it forms lithium super oxide Li 2 O 2 in case of organic electrolyte.

Finally, the reduced species whatever is formed combined with the diffused lithium ions. So, lithium reacts with oxygen and it forms Li 2 O 2. So, that is the discharge reaction that is going on. So, very simple reaction, but it is difficult to get a meaningful capacity out of this system.

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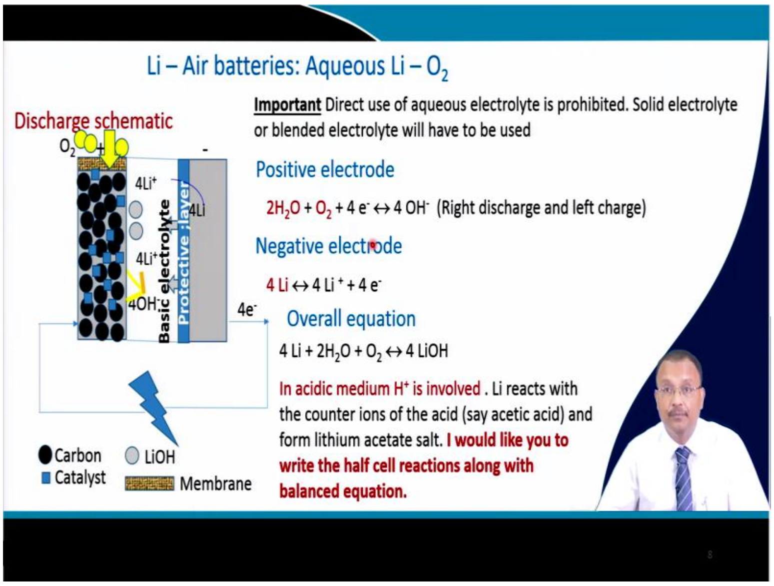

Li – Air batteries: Aqueous Li – $O_2$

Discharge schematic

**Important** Direct use of aqueous electrolyte is prohibited. Solid electrolyte or blended electrolyte will have to be used

Positive electrode

$2H_2O + O_2 + 4\,e^- \leftrightarrow 4\,OH^-$ (Right discharge and left charge)

Negative electrode

$4\,Li \leftrightarrow 4\,Li^+ + 4\,e^-$

Overall equation

$4\,Li + 2H_2O + O_2 \leftrightarrow 4\,LiOH$

In acidic medium $H^+$ is involved . Li reacts with the counter ions of the acid (say acetic acid) and form lithium acetate salt. **I would like you to write the half cell reactions along with balanced equation.**

● Carbon
■ Catalyst
○ LiOH
▨ Membrane

So, this is the schematic. So, this is the discharge schematic. So, you can see that this is the positive electrode and this is the membrane where from the oxygen, this yellow circle they diffuses through. It has catalyst also which is evenly distributed inside the porous carbon matrix, and then you are connecting the positive electrode with the negative electrode.

So, in positive electrode you have first I have considered that aqueous electrolyte is there in between. So, as I have said earlier the direct use of the aqueous electrolyte is prohibited solid electrolyte or bended blended electrolyte will have to be used otherwise lithium will not survive. So, some kind of protective layer is there which is porous for the lithium ion to pass through.

So, this should be porous enough, but some kind of protection is needed. So, if you are considering a base electrolyte, then the positive electrode this reaction it forms hydroxyl ion. So, electron is coming from the negative electrode part and water and oxygen is diffusing from the ambient. So, this is the discharge reaction during discharge it forms. So, the right arrow is the discharge and left is the charge reaction the reverse reaction. So, this convention is followed throughout the lecture.

$$2H_2O + O_2 + 4\,e^- \leftrightarrow 4\,OH^-$$

In negative electrode, it is oxidation of lithium. So, as you can see 4 electron is coming out and this 4 electron is going here. So, overall reaction is lithium and water and oxygen they form lithium hydroxide. So, lithium hydroxide is a soluble product in the electrolyte.

$4\ \mathrm{Li} \leftrightarrow 4\ \mathrm{Li}^{+} + 4\ e^{-}$

Now, if it is acidic medium then H plus ion is involved and lithium reacts with the counter ions of the acid say acetic acid you can use and form lithium acetate salt. So, I am leaving it on you to write the half cell reactions, along with the balanced equation the way I have shown for base electrolyte.

$4\ \mathrm{Li} + 2H_2O + O_2 \leftrightarrow 4\ \mathrm{LiOH}$

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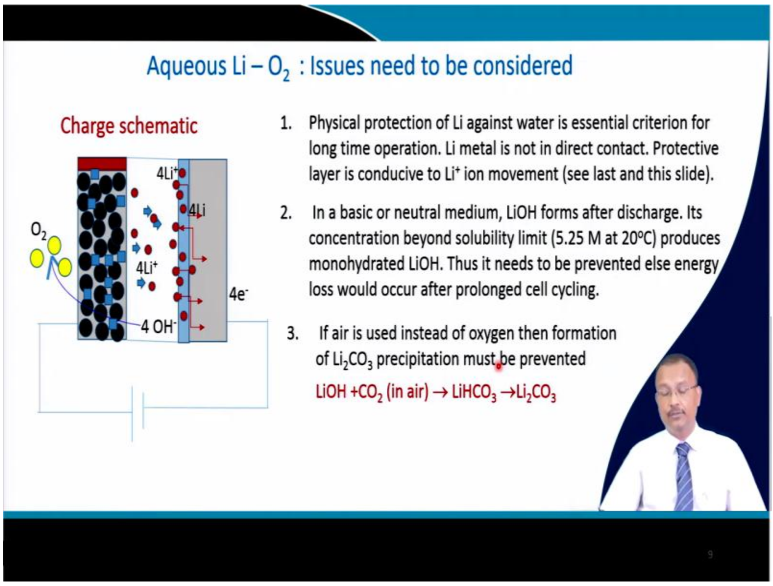

Aqueous Li – $O_2$ : Issues need to be considered

Charge schematic

1. Physical protection of Li against water is essential criterion for long time operation. Li metal is not in direct contact. Protective layer is conducive to $Li^+$ ion movement (see last and this slide).
2. In a basic or neutral medium, LiOH forms after discharge. Its concentration beyond solubility limit (5.25 M at 20°C) produces monohydrated LiOH. Thus it needs to be prevented else energy loss would occur after prolonged cell cycling.
3. If air is used instead of oxygen then formation of $Li_2CO_3$ precipitation must be prevented

$LiOH + CO_2\ (\text{in air}) \rightarrow LiHCO_3 \rightarrow Li_2CO_3$

Now, the reverse is the charge. So, this is the charge schematic. So, physical protection of lithium against water is essential criterion for long term operation. So, lithium metal is not in direct contact with the aqueous electrolyte, protective layer that is conducive to lithium ion movement. So, that already I have explained in the last slide.

So, if you consider a basic or a neutral medium LiOH forms after discharge. Its concentration beyond solubility limit is quite high 5.25 moles at 20 degree Celsius that produces monohydrated lithium hydroxide; so, extra lithium if it forms. This needs to be prevented else the energy loss would occur after prolonged cycling. What will happen that if it is not there in the electrolyte it will not participate in the subsequent charge reaction and discharge reaction.

So, slowly you will see the capacity will be losing, this battery will lose capacity. So, this must be prevented and oxygen is preferable because if you use air instead of oxygen, then carbon dioxide will start reacting with lithium and lithium carbonate precipitation that will occur. So, this occurs in two step first lithium bicarbonate forms and then forms lithium carbonate. So, this also must be prevented.

So, you will have to take two precaution; one is that concentration beyond the solubility limit that will have to be restricted for lithium hydroxide which is the reduced product. And second is, if you are using air then care must be taken, so that lithium does not directly react with carbon dioxide to form lithium carbonate.

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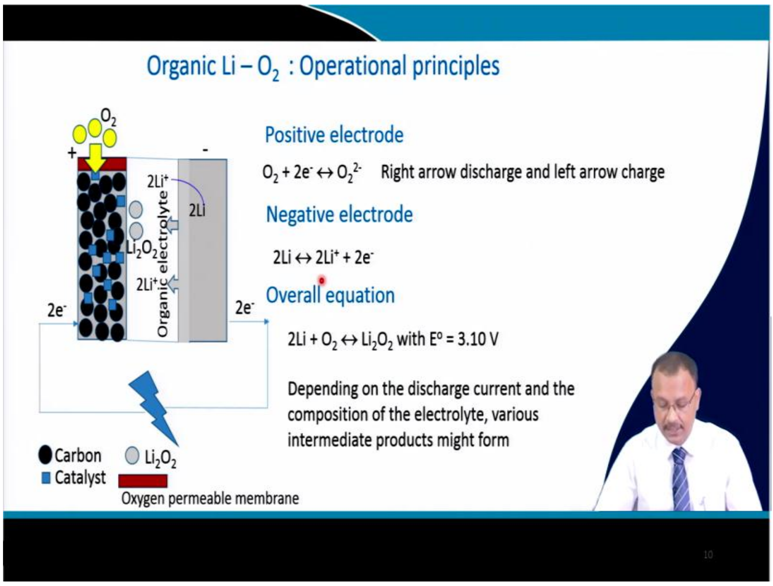

## Organic Li – $O_2$ : Operational principles

Positive electrode

$O_2 + 2e^- \leftrightarrow O_2^{2-}$ Right arrow discharge and left arrow charge

Negative electrode

$2Li \leftrightarrow 2Li^+ + 2e^-$

Overall equation

$2Li + O_2 \leftrightarrow Li_2O_2$ with $E^o = 3.10$ V

Depending on the discharge current and the composition of the electrolyte, various intermediate products might form

Now, we will talk about the organic lithium-oxygen type of cell. So, here the same kind of schematic is there, but the reaction scheme is different. So, here also you have a permeable membrane where from oxygen is coming and you have porous carbon and some catalyst is there. So, this catalyst eventually helps the over voltage that you get, it reduces the over voltage we will talk about that.

So, in positive electrode during discharge it forms these peroxide ions and in negative electrode lithium gets oxidized. So, overall reaction is pretty straight forward and this value of E 0 is about 3.10 volt. Remember, when we calculated the theoretical energy density we took this value we assumed that we are using organic electrolytes. So, we took this value which is about 3.10 volt.

$O_2 + 2e^- \leftrightarrow O_2^{2-}$

$2Li \leftrightarrow 2Li^+ + 2e^-$

Overall:

$2Li + O_2 \leftrightarrow Li_2O_2$ with $E^o = 3.10$ V

Now, depending on the discharge current and the composition of the electrolyte whatever you are using, various intermediate products form. So, that is one caution. So, not always this will form, although this is the most known product that forms during the discharge reaction, but several intermediate product might also form during this reaction.

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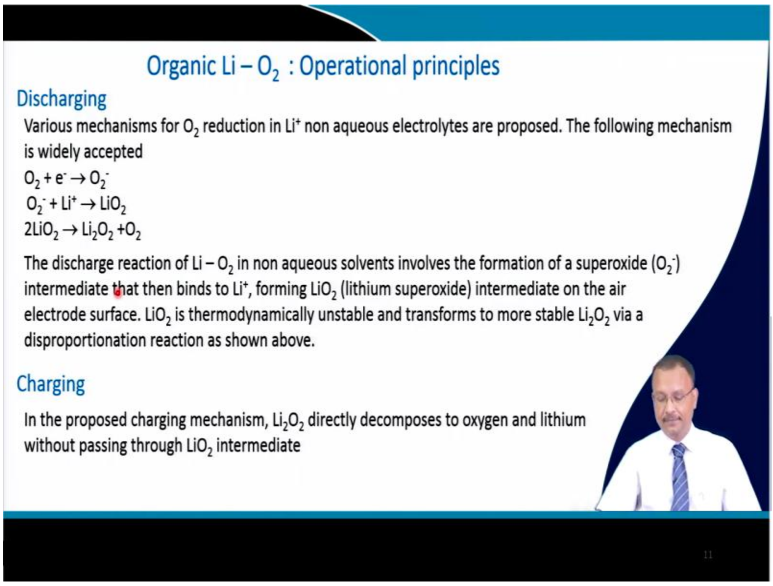

## Organic Li – $O_2$ : Operational principles

### Discharging

Various mechanisms for $O_2$ reduction in $Li^+$ non aqueous electrolytes are proposed. The following mechanism is widely accepted

$O_2 + e^- \rightarrow O_2^-$

$O_2^- + Li^+ \rightarrow LiO_2$

$2LiO_2 \rightarrow Li_2O_2 + O_2$

The discharge reaction of Li – $O_2$ in non aqueous solvents involves the formation of a superoxide ($O_2^-$) intermediate that then binds to $Li^+$, forming $LiO_2$ (lithium superoxide) intermediate on the air electrode surface. $LiO_2$ is thermodynamically unstable and transforms to more stable $Li_2O_2$ via a disproportionation reaction as shown above.

### Charging

In the proposed charging mechanism, $Li_2O_2$ directly decomposes to oxygen and lithium without passing through $LiO_2$ intermediate

So, there are various mechanisms that has been proposed. So, the study material whatever I have suggested they have illustrated this separate reaction mechanism. So, I will just give you the highlight of it. So, there are various mechanisms for oxygen reduction in lithium plus non aqueous electrolytes.

So, one of the most widely accepted mechanism is something like this. Initially oxygen gets reduced to the peroxide form sorry, peroxide forms and this peroxide that reacts with lithium ion to form an intermediate product LiO 2 and then this LiO 2 dissociates to Li 2 O 2 anode.

$O_2 + e^- \rightarrow O_2^-$

$O_2^- + Li^+ \rightarrow LiO_2$

$2LiO_2 \rightarrow Li_2O_2 + O_2$

So, the discharge reaction of this non aqueous solvent involves the formation of a superoxide O 2 minus. This is termed as superoxide. So, that superoxide intermediates that binds with lithium ions here. So, it forms an lithium superoxide intermediate on the air electrode surface that is the positive electrode surface.

So, thermodynamically it is unstable and it basically transform into more stable Li 2 O 2. So, this is via a disproportionate reaction and this is one of the most widely circulated mechanism. During charging the proposed charging mechanism, this directly decomposes to oxygen. So, whatever is forming this directly decomposes to oxygen and lithium and this intermediate compound usually not detected.

So, it directly dissociates to lithium ion oxygen and this intermediate does not form which is forming during discharge reaction. So, this is one of the most common mechanism that one can find out after such studying the various literature reports. So, as you can understand this is a very straightforward reactions if you think in terms of the mechanism is concerned, but it is not that easy to construct the cell or get good electrochemical performance.

Lithium is first reacting with oxygen to form this Li 2 O 2 during discharge and during charge it is dissociated back into lithium ion oxygen. So, that is oxygen breathing battery.

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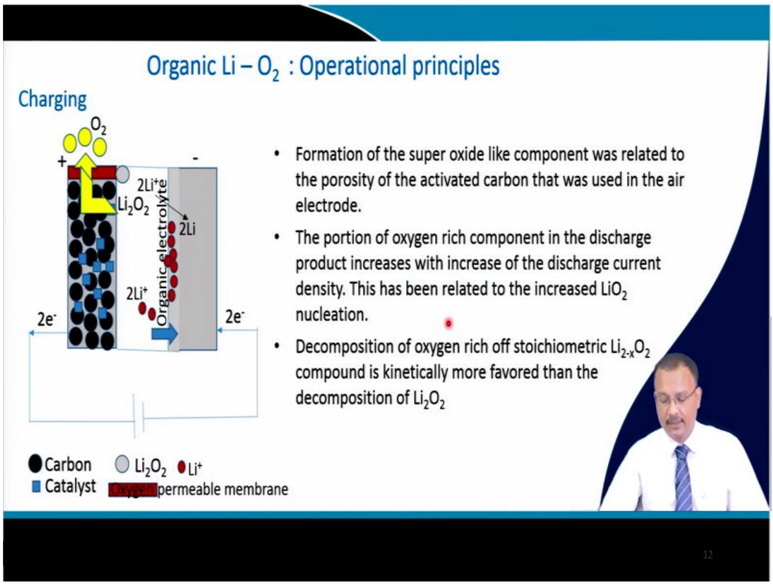

## Organic Li – $O_2$ : Operational principles

- Formation of the super oxide like component was related to the porosity of the activated carbon that was used in the air electrode.
- The portion of oxygen rich component in the discharge product increases with increase of the discharge current density. This has been related to the increased $LiO_2$ nucleation.
- Decomposition of oxygen rich off stoichiometric $Li_{2-x}O_2$ compound is kinetically more favored than the decomposition of $Li_2O_2$

So, the operational principle for charging is the formation of this superoxide like component that was related to the porosity of the activated carbon that was used in air electrode. So, this is very important this Li 2 O 2 whatever is forming here, this is the Li 2 O 2. So, this forms a some kind of layer which is non-conducting and this depends on the porosity; this porosity of this positive electrode, right.

So, this will in fact, block. How it will form in one of my lectures in this particular module when I will do the case study you will see that the way this lithium oxide Li 2 O 2 that basically covers this porous region that will decide the capacity and the electrochemical performance.

Now, the portion of oxygen rich component in the discharge product increases with the increase of the discharge current density. So, this is of course, dependent on the discharge current density. So, rate performance whenever you will study you will see their effect on the on the capacity of this kind of battery. So, this has somehow been related to the formation of this intermediate compound LiO 2.

And, finally, the decomposition of oxygen rich off stoichiometric that is not really Li 2 O 2, but little bit lithium deficient Li 2 minus X O 2. This is kinetically more favored than the decomposition of Li 2 O 2. So, these are all experimental observation and why exactly it forms like this at least I could not find the proper explanation because still it is in the research stage.

But, it is well understood that the porosity of the positive electrode then the current density that we are using that grossly affect this reaction product whether it is intermediate LiO 2 or it is Li 2 O 2 or it is lithium deficient Li 2 minus X O 2. And eventually they get during charge they get separated. So, all these affect the electrochemical performance.

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## REFERENCES

- **Christian Glaize and Sylvie Genies** “Lithium batteries and other electrochemical storage systems, Chapter – 10 page 287 – 295 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 page 183 – 185 (Study material)

So, this particular topic this has been taken from this two book. This book you know chapter 10 the page number is given and this book by P K Shen this is he is the editor and it has got a nice description about this fundamental principles. So, this you will have to read along with this lecture.

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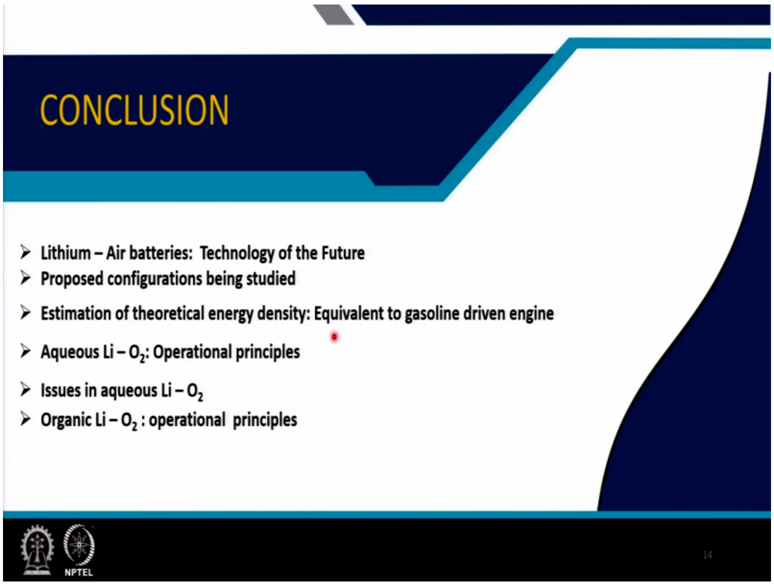

CONCLUSION

- Lithium – Air batteries: Technology of the Future
- Proposed configurations being studied
- Estimation of theoretical energy density: Equivalent to gasoline driven engine
- Aqueous Li – $O_2$: Operational principles
- Issues in aqueous Li – $O_2$
- Organic Li – $O_2$ : operational principles

So, in this particular lecture, we talked about lithium-air batteries and this is I consider technology of the future, lot of works we will have to do and many of the mechanisms is not yet well understood. Then, proposed configuration which is being studied; I told that four different configurations and they are dependent on the electrolyte that is being used whether it is aqueous or organic or polymer based solid state electrolyte or a blended electrolyte. So, based on that this demarcation is there I mean the classification is there.

Then we made an attempt to estimate the theoretical energy density and it is almost equivalent to gasoline driven engine and that is the thrust of the motivation of doing research in this area. Then we talked about the aqueous lithium-oxygen battery, what are the operational principle, what kind of reactions are involved in half cell reactions in anode and cathode and then the overall reactions.

Same thing applied for the organic base electrolyte and what are the issues in aqueous lithium-oxygen battery that I have highlighted.

Thank you for your attention.