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> Module - 11 Li - Air batteries Lecture - 42 Electrolytes for Li - O<sub>2</sub> Batteries

Welcome to my course Electrochemical Energy Storage. We are talking about Lithium-Air Battery part of module number 11. And this is lecture number 42 where I will exclusively talk on electrolytes for lithium-oxygen batteries.

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So, types of electrolyte first we will talk about. So, we are concentrating in this part. And already I have introduced aqueous and non-aqueous electrolyte. And then we will talk about in case of organic electrolyte, and the alkyl carbonate, ether and dimethyl sulfoxide based electrolyte, what are their positive and negative points.

Then we will also talk about the ionic liquid and solid state electrolyte. And finally, the salts that are used in the electrolyte, and the binder that is that you use what are their roles. So, this will be described in this particular lecture.

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So, usually four types of electrolytes are used that already you know. The first one is aqueous electrolyte; it could be either basic or acidic. In case of basic lithium hydroxide is the reaction product; in case of acidic I asked you to write the half equation and overall equations.

Then we have organic electrolyte. Then we have dual electrolyte where the positive electrode has aqueous electrolyte; and in the negative side, it has organic electrolyte. These two types of electrolyte they are separated by a solid electrolyte, and finally, polymer or ceramic base electrolyte.

So, first let us have a look of aqueous electrolyte. So, electrolyte which are aqueous and positive electrode observes interaction among gas, oxygen is involved, liquid electrolyte is involved, and solid where you have the positive electrode carbonaceous material based so that solid is also involved.

So, oxygen in the gaseous phase that convert combines with the electrons from carbon right, carbon electrode or catalyst is also there in this part, so that combines with the electron from the carbon electrode or catalyst in an aqueous electrolyte. So, the reaction is H 2 O, oxygen, and the electron which is coming from the negative electrode, so that forms this hydroxyl ions on discharge. So, this hydroxyl ions they are basically dissolved in the aqueous solution.

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If you consider the non-aqueous electrolyte, so in case of non-aqueous electrolyte interaction between the organic electrolyte and the solid, that is shown schematically here. So, oxygen as you can see in the electrolyte solution that is combined with the electrons from the carbon or catalyst system and lithium ions in the electrolyte.

So, this can be noted that the reaction product is either Li 2 O 2 mostly or this intermediate product Li 2 O that is not soluble in the electrolyte, and it forms basically a thin deposit on the surface of the positive electrode. So, this reacts Li ion and oxygen once it get reduced, so this two reacts to form this kind of thin layer.

Then mass of the carbon that is used in calculating the specific capacity, so that is a common practice that the carbon layer whatever you are using that actually you also consider when you calculate the specific capacity the way I calculated with or without oxygen, so the mass of carbon is also included there. The solubility of oxygen in organic electrolyte increases if that is the case, then the specific capacity of the cell also will increase.

Due to obvious reason, because the kinetics will get improved, and also the lower viscosity and a high conductivity of the electrolyte, so high lithium ion conductivity and the low viscosity that ensure better lithium ion diffusion towards the positive electrode. So, this you should keep in mind. So, the viscosity of the electrolyte should be optimized

and conductivity of the electrolyte is also another major factor that gives good reasonably good electrochemical performance of these batteries.

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Now, stability of the electrolyte that is a severe challenge for the development of lithium oxygen cells. And as I mentioned this is still in the research scale, it is not yet been commercialized. Although there are many market players, I will show you in my next lecture that who are the major companies they are working rigorously with this battery system.

So, the first is electrolyte should be tolerant to highly oxidative environment for desirable cycleability and decomposition of Li 2 O 2 reversibly. So, for that the electrolyte they should withstand this oxidative environment. Electrolyte also affects the oxygen reduction reaction ORR which I talked about when oxygen takes electron in the positive electrode.

And also oxygen evolution reaction which is abbreviated as OER when lithium oxygen Li 2 O 2 dissociate oxygen comes out. So, electrolyte basically will affect both these reactions. Many, many electrode electrolyte are proposed. So, there are number of papers have been published in recent times. Most popular I think are mostly the well-known carbonates the cyclic and linear type and ether based electrolyte.

So, you can have a look of this particular paper The Critical review on lithium-air battery electrolyte which is little bit old, but it gives a nice account of the type of types of electrolyte that people are using for lithium-oxygen batteries.

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So, first let us see the alkyl carbonates. So, this includes a combination of ethylene carbonate, propylene carbonate and dimethyl carbonate. So, as you can understand that already I have described it for lithium-ion batteries also this types of solvents they are used because of their stability and low volatility, they have lower vapor pressure. But unfortunately these carbonates are unstable for lithium-oxygen cells.

So, the discharge reaction as I have mentioned, it produces the superoxide O 2 minus intermediate. Now, you have the anion radical that is the ring opening agent because this is the cyclic solvents. So, they are the ring opening agent for the carbonate, and they form this kind of peroxy anion. And this eventually they are more reactive than the super oxides. So, super oxides they are reactive. But, once this anion radical they opens the ring and forms this peroxy anion, they are much more reactive.

So, finally, it results decomposition of the carbonate based electrolyte. And once they are decomposed, they form high molecular weight products like lithium alkyl carbonates, lithium carbonates they are formed. So, you are leasing lithium, so capacity will drop down. Carbon dioxide gas, they start to evolve instead of oxygen during the charging process because this is no longer a oxygen breathing battery. It is exhaust in exhaling

carbon dioxide like human being. Electrolyte decomposition also is the primary source of carbon dioxide that is formed during charging.

So, these are the side reactions which are quite complicated I have tried to make it simplified versions. So, if you read the original papers particularly the one that I referred, they have mentioned about it. So, these are the side effects and side reactions. And due to this carbonate based electrolytes, they are not considered as acceptable electrolyte for lithium-oxygen cell.

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So, what are the alternatives? Ethers, they are relatively more stable than carbonates. Ethers are stable towards the so called nucleophilic attack by the superoxide intermediates which you have seen that happen for your carbonate based electrolyte solvent. But, they have also low vapor pressure, and they have extended oxidation potential you can go up to 4.5 volt versus lithium, they are stable.

So, after first discharge, this product Li 2 O 2 together with the electrolyte decomposition form a mixture of lithium carbonate, lithium alkyl carbonate, polyether ester, carbon dioxide, H 2 O. So, it is not full proof solvent. But, as compared to the carbonate, this is less it is not that much like the carbon it is not that severe in case of ether based solvent. So, the formation of this carbonate based parasitic side products in substrate product interface and also product and electrolyte interface that eventually will

lead to high interfacial resistance and cause really very large charging over potential of Li O 2.

So, you will find that you need more voltage to charge this battery as compared to the standard voltage. So, over potential, it will raise because of the formation of this side product. And during discharge as compared to the theoretical voltage, you will see that the voltage drops down considerably.

So, increase of charging over potential beyond 4 volt that will eventually cause again electrolytic decomposition. So, it is a viscous circle. So, subsequent cycles when you do repeated charge and discharge, you will find that the capacity fade cannot be avoided.

So, within subsequent charge and discharge over potential will happen. So, you will have to increase the voltage beyond 4 volt. So, electrolyte decomposition will be more severe cycle by cycle, and in the subsequent cycle. So, eventually the capacity fade will be there. So, in view to this neither carbonates nor ether based electrolyte are proven to be stable for lithium-oxygen rechargeable cell. Unfortunately, this also does not qualify well for a stable electrolyte system.

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And I am talking about the solvent as you can understand. Then dimethyl sulfoxide, so this is abbreviated as DMSO. This electrolyte demonstrates better stability as compared to the earlier two carbonate and ether based electrolytes. Higher vapor pressure, this material decreases their validity as electrolyte for lithium-oxygen cells. So, at higher temperature, they are not that effective. Small amount of side products formed from decomposition of DMSO solvent. So, that is DMSO 2, Li 2 SO 3 as well as lithium sulphate when particularly carbon electrode is used. So, there also this decomposition problem is there.

And this electrolyte this solvent based electrolyte they also interact with lithium metal anode. So, lithium metal anode requires a protection from the electrolyte, else the internal resistance increases and specific energy of the cell decreases because of the loss of capacity. And also voltage fading cannot be avoided. So, eventually it will retard I mean it will deteriorate the specific energy of the cell.

So, it is a real challenge although the reaction is quite straight forward. But, as you can see due to the operational mechanism, due to the formation of O 2 minus this peroxide, the superoxide ions, anions, and due to the non-conductivity of the reaction product the discharge product Li 2 O 2, this is not a very good system to work with.

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Then people have also tried ionic liquid. And ionic liquid has one advantage it has wide potential window and negligible vapor pressure. So, you can safely increase the operational temperature. It has high ionic conductivity as well as hydrophobicity. So, application of ionic liquids are basically limited because of their poor lithium-ion solubility so that is one thing. And also at room temperature ionic conductivity is not that great.

Now, this oxygen reduction reaction mechanism in ionic liquid electrolyte that involve Li 2 O 2 formation from the chemical decomposition reaction of Li O 2. So, the way we explained in case of carbonate base solvent or ether base solvent, this intermediate product is also detected in case of ionic liquid. So, imidazolium based ionic liquids, they are not stable enough against the reduction at lithium deposition potential. And this is not very use useful to be used for with the lithium metal anodes.

But, the ionic liquid based on pyrrolidinium or piperidinium, they are fairly stable against peroxide radical attack, but eventually more research is needed to judge the suitability of ionic liquids in lithium oxygen rechargeable cell. But, this is a good area to do further research that what are the ionic liquids they are, particularly suitable for this types of batteries.

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Then we have solid state electrolyte that also people have started to work on. They are actively being studied mainly for the safety, durability, wide operation range, potential range is also quite large. And they also prevent the lithium dendrite formation. Lithium dendrite formation, as you know once you use the pure lithium, then this formation of lithium dendrite is almost inevitable. Major drawback is lithium ion conductivity, they are not that great. The system of interest is lithium metal active layer. Then you have a lithium ion conducting polymer buffer layer.

Then a water soluble LTAP protective layer, so that is a NASICON type Li 1.35. So, this should be subscript, aluminium 0.25, titanium 1.75, sulfur 0.3, phosphorous 2.7, oxygen 12. So, this is abbreviated as LTAP. This is basically a glass ceramic. So, that protective layer is there. Then you have this acetic acid, water and Li O A s A c based electrolyte. Then you have carbon air cathode which includes super fine platinum particles that is that acts as a catalyst, typically 1 to 4 nanometer.

So, say see the electro chemical chain starting from lithium, then you need a protecting buffer layer which is a glass ceramic, then this is aqueous electrolyte, then carbon air electrode system which also includes this catalyst for a effective ORR reactions. So, this is a pretty complicated system.

So, for this kind of system a flat discharge and charge plateau was achieved, but this is quite poor 225 milliampere hour per gram and that has been used when you use 56 percent of this acetic acid based electrolyte.

And the current density the c, the current that is used that is also quite low 0.5 milliampere per centimeter square, 60 degree Celsius under 3 atmosphere of air, so it is a pressurized air that has been used for the better oxygen diffusion. So, this is not that great, but it is one of the most cited literature report.

And this lithium oxygen cell retained the discharge charge capacity 250 milliampere per gram within 15 cycles. So, 15 to 20 cycles, it survives. Then due to the production of so many things, it eventually capacity fade cannot be avoided.

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Another workable system is relatively simpler lithium metal anode is there. Then a solid electrolyte in terms of LAGP, lithium aluminium germanium phosphate, this is solid electrolyte. And then this LAGP coated CNT, so this is used as because electrolyte is there in case of your carbonaceous positive electrode as well which is porous in nature. This exhibits a better discharge capacity 1500 milliampere hour per gram at this rate 200 milliampere per gram.

Capacity retention is less than 20 percent between this voltage. So, it is not good that you can see that capacity retention within a few cycles this is less than 20 percent. But, the rate performance is quite good. So, even if you go for 10 ampere per gram, you get capacity out of these cells and that is mostly explained because CNT that acts as a catalyst as well as conducting path for the electrons.

So, LTAP and a mixture of single wall carbon nanotube and imidazolium based ionic liquid is used as the gel cathode. You can just try to understand that several combinations of electrolyte, then electrolyte in the positive electrode particularly the gel type of electrode that also people have tried. Although as I mentioned imidazolium is not a very stable ionic liquid.

But, for this particular system, discharge capacity was relatively high; the cell withstand about 100 charge discharge cycles. And maintaining 2000 milliampere hour per gram. So, here also the discharge product is Li 2 O 2, and converted chemically to Li OH, and

Li 2 CO 3 reacting with moisture and carbon dioxide in air. So, that is another problem that you will have to protect that thing as well. And that puts a big question mark.

So, always we will have to use only oxygen from the oxygen cylinder or if I try to use air oxygen in air, then due to the presence of carbon dioxide and moisture in air, we will have to have a suitable mechanism, so that my discharge product that should not get reacted with this to form something else, and in the process I lose lithium. So, these are the challenges for these batteries.

So, the associated problems are lack of flexibility towards large volume change in discharge and charge cycles. So, that is there you know that many of the material like silicon and metal anode based, metal alloy based anode material also is having this problem of volume expansion. Apart from that, low electrode electrolyte interface and low lithium ion conductivity that also needs to be solved for this solid state electrolytes.

Another problem is this high valence transition metal cation that can be reduced by lithium. So, they uses this transition metal cation during this process of making this solid state electrolyte. So, if lithium reduces this thing, high valence to lower valence state that is a problem. Apparently the mechanical strength is also a problem. Ease of fabrication, cost these are the factors that one should actually consider before they go for this kind of solid state electrolyte.

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Now, we will talk about the electrolyte salts and binders that is used. So, superoxide ions they are responsible for the decomposition of binder as well and electrolyte like we described earlier. For example if you use this common salt Li PF 6 they are decomposed during the discharge cycle. So, Bis oxalate borate abbreviated as LiBOB in PC also reacts with superoxide radicals to form lithium oxalate in discharge product.

So, this oxygen which is being created that always try to attack the other constituents and form the decomposition product. So, lithium salts also react with Li 2 O 2 during discharge cycle. Additionally Li 2 O 2 is contaminated with decomposed halide species.

So, this species is also dangerous. So, halide species that basically originates from lithium chlorate perchlorate LiBF4, Li PF 6 and LiTFSI, so that also needs to be inhibited. So, in one of the studies, this LiTFSI that has been dissolved in six different non-aqueous solvents as electrolyte. And PTFE was the binder in that case, binder that was also dissolved. So, Li F was found in the discharge product of the cell. So, it reacted with this lithium salt and this could be due to the decomposition of binder or the lithium based salt.

PVDF binder this is also proved to be unstable. Once you try to use a non fluorinated solvent lithium salt like LiBCN 4 that is used with PEG polyethylene glycol, dimethyl ether and tetraglyme as the electrolyte.

So, the cell cycles and fluorine is detected because of the decomposition of PVDF binder in Li O 2 environment. So, that is also a problem that this O 2 minus ion they also reacts with this salt that we are using in the electrolyte apart from the solvent also salt is also having a stability problem.

Free standing binder free air electrode if you use that would resolve the binder decomposition problem that is there. The binder you will have to use any way to bind this carbonaceous material. But, truly stable electrolyte for Li O 2 is yet to be found. So, still lot of research is required for its solvent, for the salts, for the binders, for all these components because it is a oxidative environment, so one should be very, very careful.

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So, this part of the lecture again it is taken from these two books what I mentioned earlier as well, and the page number for the study material this is also mentioned.

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So, in this particular lecture, we talked about types of electrolyte, aqueous and nonaqueous electrolyte we talked about. Then what are the desirable characteristics of the electrolyte. Then finally, we talked about the solvents, alkyl carbonates, then ether and dimethyl sulfoxide, then ionic liquids and solid state electrolytes, and finally, electrolyte salts and binders. Thank you for your attention.