**Electrochemical Technology in Pollution Control**

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**Lecture - 33**
**Batteries and fuel cells**

Greetings to you all, happy new year to you. We have been discussing about the Batteries. And I had shown you that air cell battery in the last class and there I had told you that there could be peroxyl decomposition and we will take a look at it of in the next class. So, I had shown you this discussion.

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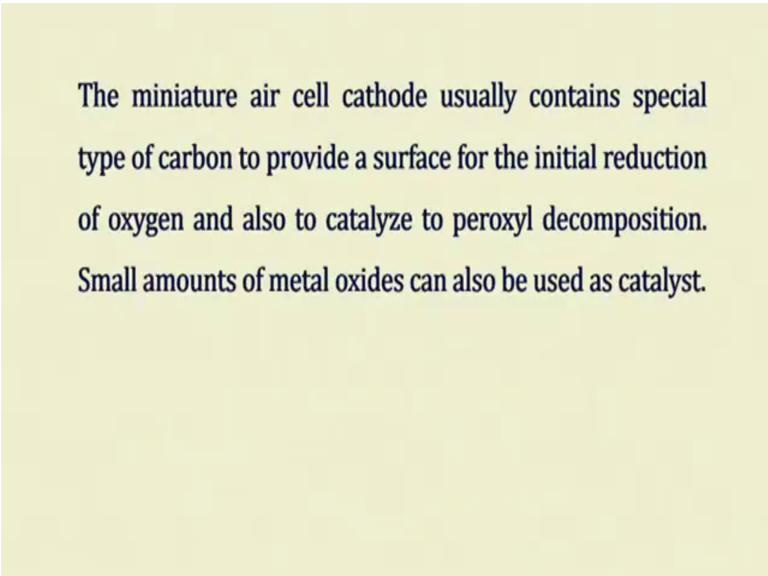

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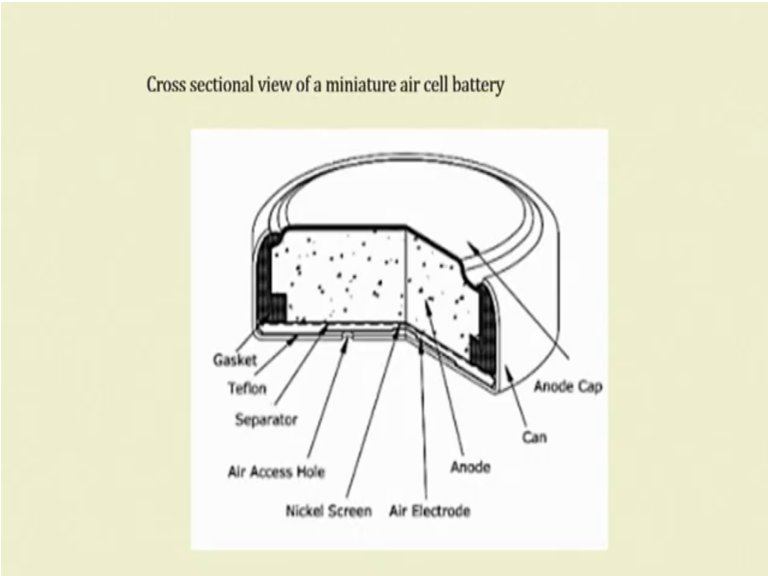


And then I had showed you this figure which contained nickel screen, air electrode, anode, cathode and all these separator. This is the separator, gasket, Teflon etcetera. This I had already shown you.

So, the miniature air cell cathode regarding this I had explained to you that we are talking about peroxyl decomposition. How it will happen, we will discuss in the next class like that I had already conveyed to you.

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| Sr. No. | Battery system | Working voltages | Energy Density Wh/L | Specific energy Wh/Kg | TemperatureRange, $^0C$ |
|---|---|---|---|---|---|
| 1 | Carbon-Zinc($Zn/MnO_2$) | 1.2 | 70 to 170 | 40 to 100 | -40 to +50 |
| 2 | Alkaline - Manganese dioxide ($Zn/MnO_2$) | 1.2 | 150 to 250 | 80 to 95 | -40 to +50 |
| 3 | Zinc- Mercuric oxide($Zn/HgO$) | 1.3 | 400 to 60 | 100 | -40 to +60 |
| 4 | Zinc- Silver oxide($Zn/Ag_2O$)($Zn-Ag_2O$) | 1.55 | 400 to 520 | 130 | -40 to +60 |
| 5 | Zinc/Air($ZnO_2$) | 1.25 | 700 to 800 | 230 to 400 | -40 to +50 |

Now, here there is a sort of summary of the battery systems what we have so far discussed. So, first one is carbon-zinc and zinc MnO2 mixture that gives you a working voltage of about 1.2 volt. These kind of things you always get it in the market. Approximately whenever you go and buy torch cell you will always end up they would have written that 1.2 volts is the working voltage. And energy density this and all they will not write energy density and specific energy watt hours per kg or temperature etcetera, but this is more than enough for regular marketing technology.

So, with this, but for comparison this 1.2 will not be varying much for different voltages for different batteries. Usually 1.2, 1.2, 1.3, 1.25, 1.55 like that we will get voltages, but what varies is here on the energy density and temperature range and specific energy that is watt hours per kg.

So, for carbon-zinc battery, we will be working with we will be getting about energy density of 70 to 170 watt hours per litre. And specific energy will be 40 to 100, this temperature range working temperature range should be minus 40 to 50 which means that they are you are comfortable using it in almost all kinds of a environment, except maybe in the arctic where there may be temperatures of less than 40 or something.

So, an improvement over this is alkaline manganese dioxide and zinc MnO2. This alkaline manganese dioxide is the electrolyte and zinc. And zinc is an electrode and MnO2 is another electrode. So, here also working voltage is 1 is to 2, but here you can see the difference from 170 to it has gone up to 250.

So, a specific energy would be slightly less compare to this carbon zinc battery. And working temperature is almost same in almost all cases. Now, look at the third one, zinc and mercury oxide that gives you about 1.3 volts and 400 to 60. And specific energy is about 100 and minus 40 to 60 is the working temperature.

Zinc silver oxide these are very common batteries smaller size, but the voltage will be 1.55. You can look at the energy density that is also 400 to 520 specific energy is approximately one third. Here you do not see much change in the first four first. And only in the zinc air oxide; zinc air and zinc oxide you will end up with a voltage energy density specific energy would be 230 to 400 that is a an improvement. Energy density is also 700 to 800 watt hours.

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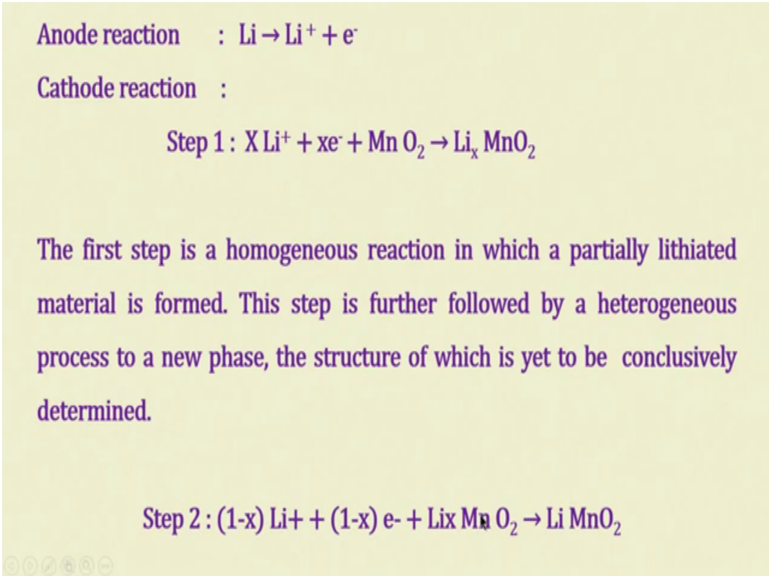


So, what is the anode reaction in such cells? Nowadays, we talk about lithium batteries quite a lot and these lithium batteries I want to spend some time with you, regarding explaining the anode reactions and cathode reactions. So, the anode reaction is basically a very simple one lithium to lithium ion plus electron. And cathode reaction, there will be lithium ion and electrons the combining the electron and the MnO 2 is there. So, this MnO2 is in the form of a paste and what we end up is Li x MnO 2. X is number of moles. So, X moles of lithium will react with x mole of electrons and MnO 2 to give you Li x MnO 2.

So, the first step is a homogeneous way this is a very homogeneous reaction. In which a partially lithiated material is formed, that is the electron is gone, but some amount of lithium is always there cation and that is known as partially lithiated material. So, this step is followed by a heterogeneous reaction involving manganese dioxide paste.

So, that is a new compound formation which is something like a solid state chemistry that is happening there. So, the x in Li x MnO 2 here in this slide, this x is sort of not fixed. So, the proportion of lithium to MnO 2 will keep on varying that is why, but it is a solid state reaction.

So, the structures of what actually Lix MnO 2 is we do not know, we have to take the scanning electron microscope and other x ray methods to determine the actual structure of the complex that is formed. And that is only part of the system there is one more reaction that is happening that remaining lithium will be 1 minus x and the same number of electrons will also be there. And that will react with the Lix MnO2 to give you Li MnO2 the composition of this Li MnO2 is fixed that is a well-defined material.

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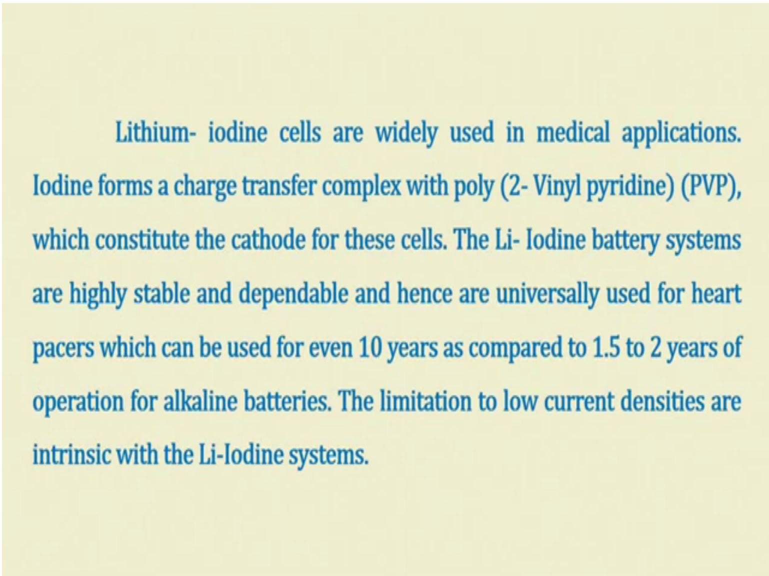


So, the lithium MnO2 we have discussed, but then there are other kinds of cells that is the lithium iodine cells. So, here instead of MnO2 we are going to use iodine. So, lithium iodine cells are widely used in medical applications. So, iodine also forms some sort of a charge transfer complex with poly 2 vinyl pyridine PVP, it is known very commonly which constitutes the cathode for such cells, it is not the iodine, but it is the PVP. So, the charge transfer complex is something approximately sort of not very well defined again. It is the same molecule in which the electrical charge density will be more towards one part of the molecule than in the other part.

So, the charge transfer the iodine is well known for that, lot of iodine complexes are charge transfer complexes. That means, there is no stoichiometric new formation compound formation, but there will be some sort of a typical chemical reaction in which the colour of the solution or some properties related to the electron density will be changing a little bit.

So, the lithium iodine battery systems are basically very stable. And they are therefore, they are dependable that is why they are used in the in the medical field. So, here I have written that universally used for heart pacers. Why do we need highly stable and dependable batteries lithium iodide batteries for heart patients? I think anybody can understand what is the required because the heart has to keep on beating.

So, the possibility of failure should be very less. So, it must work for a number of years together, but what is required is a very small amount of current. So, that the machine heart like battery, if it is an implanted in the body it will keep on working for long time, and I have heard doctors say that do not worry about the implant it will work for at least 10 years 15 years. By that time we will see if anything any problem comes and then that even 10 years of life expanded using a small lithium iodide battery itself is the great advance. Because compared to other batteries know, alkaline battery even including alkaline batteries 1.5 to 2 years is the optimum life.

Afterwards the current will start slowing down and they will be not be able to draw the current from the same battery we have to change the battery. So, for long term working lithium iodide batteries are the best. So, the limitation to low current densities, what we are drawing I had shown you in the table; it is intrinsic with the lithium iodide systems.

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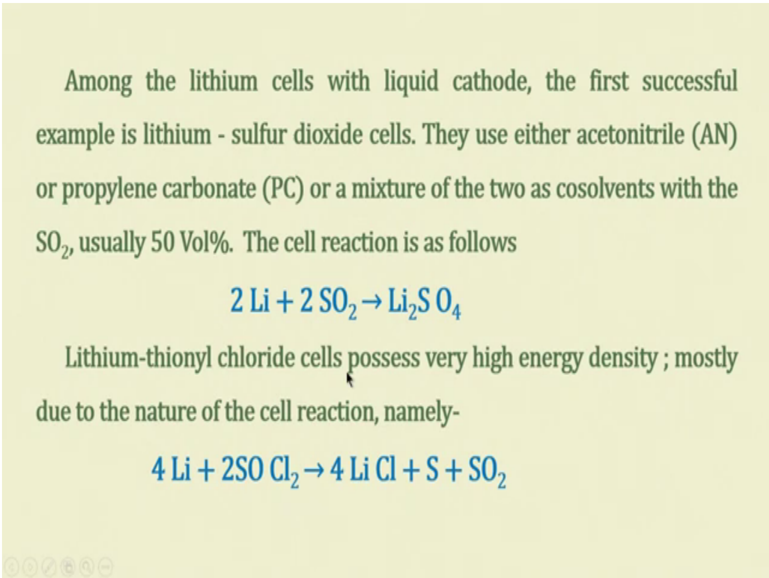


So, among the lithium cells there are number of other variations I can say. So, the one can be with liquid cathode and some can be you know paste a paste cathode. And then sometimes I have seen even in plastic papers the lithium paste is coated and then that itself will serve as a cathode.

So, the first successful example of such cells is lithium sulfur dioxide, you may be wondering why sulfur dioxide? Sulfur dioxide is a gas at room temperature, but if we include sulfur dioxide as a air battery or something like that the we have to use acetonitrile or poly propylene carbonate or a mixture of these two as co solvents with the SO 2. That means, sulphur dioxide is usually dissolved in poly propylene carbonate and acetonitrile as a solvent that is a solvent and then lithium part remains the same.

So, the mixture of the two solvents should be approximately 50 percent by volume. So, the what would be the cell reaction in such cases? See PVP does not react. And acetonitrile does not react and there is no chance for oxidation or reduction; so, only the SO 2.

So, SO 2 must react with the lithium to produce something what is that something look at the slide now, 2 lithium and 2 SO 2. It is very simple straightforward compound lithium sulfate, any SO 2 for that matter will react with the metal to give you sulfates. So, another possibility is lithium thionyl chloride batteries, that is SO CL 2 thionyl chloride is a very standard chemical in almost all organic chemistry laboratories. So, if I use thionyl chloride containing li. So, it contains; so, SO 2 basic formula is the SO CL 2 not SO 2 as such. So,, but basically it is made using sulfur dioxide and chlorine HCl.

So, they possess very high energy density mostly due to the nature of the cell reaction. Again here I write 4 moles of lithium will react with 2 moles of SO CL 2 to give you 4 lithium chloride 4 times lithium chloride plus sulfur plus SO 2 that is the ultimate reaction.

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| Sr. No | Cell systems | Working Voltage, V | Energy Density, Wh/L | Specific energy, Wh/L | Temperature range of operation, ⁰ |
|---|---|---|---|---|---|
| (A) Solid Cathode Systems | | | | | |
| 1 | Li/CF | 2.5-2.7 | 400 | 200 | -20 to +60 |
| 2 | Li/$MnO_2$ | 2.7-2.9 | 400 | 200 | -20 to +55 |
| 3 | Li/$I_2$ | 2.4-2.8 | 920 | 250 | 37 |
| 4 | Li/Fe $S_2$ | 1.3-1.7 | 460 | 250 | -20 to +60 |
| (B)Liquid cathode systems | | | | | |
| 5 | Li/$SO_2$ | 2.7-2.9 | 440 | 250 | -55 to +70 |
| 6 | Li / SO $Cl_2$ | 3.3-3.5 | 950 | 300 | -50 to +70 |

So, here I am giving you some sort of a system containing lithium looks fairly important. And here I have lithium and carbon and solid cathodes you know all these are solid cathode systems ok. Then this is fluoride. So, 2.5 to 2.7 is the working voltage. You just see imagine in the previous table I had shown you that the working voltages are around 1.2, but now, the this gives you 2.5 to 2.7 working voltage. That is why lithium cells are where I have assumed in great industrial importance in recent years including systems for transmission and a transport most of our buses, scooters, vehicles etcetera cars they all use lithium cells.

And the energy density is also quite high 400, specific energy is 200 and temperature range also seems to be fairly good for industrial area for hot countries as well as cold countries; minus 20 to plus 60 they work efficiently.

So, now, I can change the cathode system lithium MnO2. That gives you still slightly better 2.7 to 2.9 working voltage and they essentially same energy density and a specific energy temperature range which is also very good. Now, compare these two lithium iodide. So, what happens in lithium iodide? It is 2.4 to 2.8 voltage and energy density is 920 that is fantastic.

Specific energy is definitely remains the same, but their temperature range of operation is approximately 37 degree. This is where the catch is because any temperature variation the rate of reaction will double every 10 degrees or reduced by half 50 percent every 10 degrees reduction.

So, this lithium iodide would be useful only inside the body where our body temperature is approximately 37 degrees 37, 38 degree centigrade. Compared to that lithium Fe S 2 is 1.3 to 1.7 very ordinary approximately, but energy density and the specific energy are better compared to zinc and MnO 2 systems. So, that will be minus 20 to plus 60 working range also.

So, then suppose I use liquid SO 2 system which I had defined discussed with you earlier. If I use lithium SO 2 I get 2.7 to 2.9 voltage working voltage and 440 not bad. And 250 is the specific energy and temperature also is quite suitable. Look at SO 2 SO CL 2 thionyl chloride. I have 3.3 to 3.5 volts and the 950 is our energy density and 300 is the specific energy.

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Secondary batteries

In secondary batteries the cell reaction can be made to proceed in any direction by withdrawing or supplying the current. These secondary or rechargeable batteries may be broadly divided into the following three categories :

1. Lead acid accumulators or Acid Batteries
2. Alkaline storage batteries
3. Others including lithium/lithium ion batteries. Each of these systems are discussed below

So, this also seems to be quite good with respect to our lithium batteries. Now I want to discuss with you something about these secondary batteries. So, in secondary batteries what is the problem? The cell reaction can be made to produce proceed in any direction by withdrawing or supplying the current.

These are the things which we know which we normally use on and off on and off whenever battery whenever there is a battery is discharged we would like to make sure that the battery is recharged these are all rechargeable batteries.

So, if the we keep on working the battery when the all the energy is taken off again I connect it to a source of battery a source of electricity again the reaction will be reversed. So, it because it is a reversible cell reaction and it gets charged again. So, you can keep on using it number of times again and again and again. So, that is very convenient especially if we want to use the batteries for transport and many other reproducible applications.

So, the secondary batteries can be divided into basically several classes for example, lead acid batteries also are secondary batteries acid batteries, which we are all very familiar most of the our cars and vehicles etcetera. They work on lead acid batteries only they are still useful even though environmentally they are not very convenient.

So, look at the slide now I have three types of rechargeable batteries. One is lead acid accumulator or lead acid batteries they are also called as accumulators. And the second type is alkaline storage batteries. And then third is others other types of batteries including lithium and lithium ion batteries.

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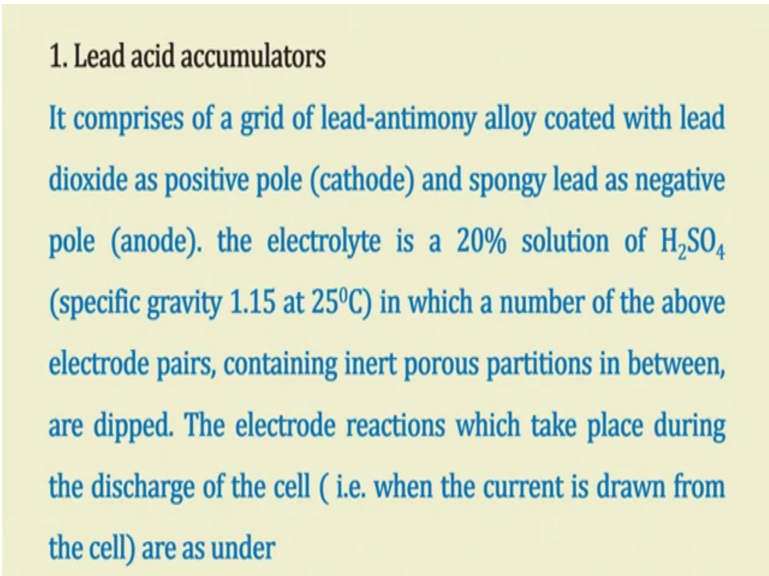

So, all these systems let us take a look at how they work. Now, lead acid accumulator as you all know is a grid of lead antimony alloy coated with lead dioxide as positive pole where that is cathode. And spongy lead as negative pole that is the anode, the electrolyte is a 20 percent solution of sulfuric acid specific gravity 1.15

Sometimes, what happens know during the reaction the lead acid battery, we the water in lead acid batteries we see we do not use very concentrated sulfuric acid in batteries. So, they are all diluted with water. So, over a period of time water gets evaporated lead gets concentrated and not lead sulfuric acid and the battery performance will come down.

So, we have to keep on topping up the water to with water to keep the lead acid battery working efficiently. So, not only that I draw about 1.2 volts, but if I want to draw more I can connect them in series and draw on more voltage. So, a number of above electrode pairs I can keep on connecting. And I can keep them separated by inert porous partitions, these are all basically silica partitions. It is called as smoked silica available in the market. And the inert porous partitions are dipped in between the electrodes. So, the electrode reactions that take place during the discharge of the cell that is when the current is being drawn basically

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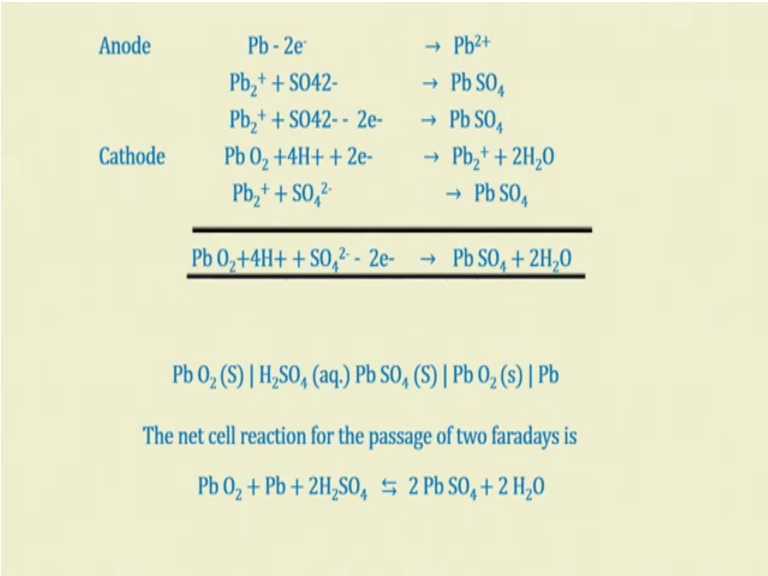


So, I have this kind of reactions lead goes to lead ions ok. So, that will lose two electrons and goes to lead ions. Lead ions will react with SO4 2 minus and that goes to lead sulfate and leads plus and SO 4 2 minus plus minus 2 minus goes to lead sulfate again.

So, these are the two reactions here there is an error I would like to make the correction here itself for your benefit.

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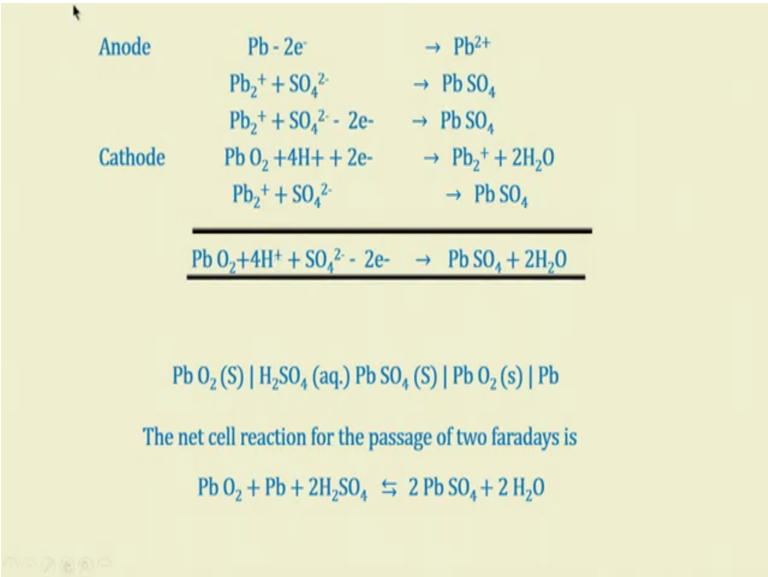


So, in the lead acid batteries basically lead will lose 2 electrons giving you lead ions. And these lead ions will work will combine with sulfate ions to give you a lead sulfate and lead sulfate Pb 2 plus also will react with one more SO 4 ions to give you PbSO 4 lead sulfate. So, at the cathode it is lead oxide in presence of acid it will be 4H plus plus 2e minus that gives you lead Pb 2 plus and plumbers and 2H2 O. And Pb plus Pb2 plus will react with SO 4 to give you lead sulfate.

So, overall reaction would be you can add them up like algebraic equations cancel right side left side etcetera whichever is common. And then you end up with an equation like Pb O2 plus 4H plus plus SO4 minus 2 electrons that will give you lead sulfate plus 2H 2O. The reactions what I have written for anode and cathode, they are all basically sort of non-stoichiometric reactions that is why you have Pb 2 single plus Pb 2 single plus SO 4 etcetera. But every time you can say you can conveniently cancel them from the real left side and right side and like an algebraic equation and write the overall equation like this.

Now, the lead acid battery how it is composed of? Lead acid battery is simple, take lead oxide that is solid powder and then they say this symbol you know. This separator H2 SO 4 containing lead sulfate and Pb O 2 again solid and another is lead that is the electrode.

So, the net cell reaction for the passage of two faradays two equivalent now, here two numbers of electrons are there. So, it is a two equivalent reaction. So, two faradays of electricity should be passed to get this reaction going. So, Pb O2 plus lead will give you two h will react with 2 h 2 SO4 giving you two Pb. SO 4 plus 2H2 O that is the total stoichiometric reaction.

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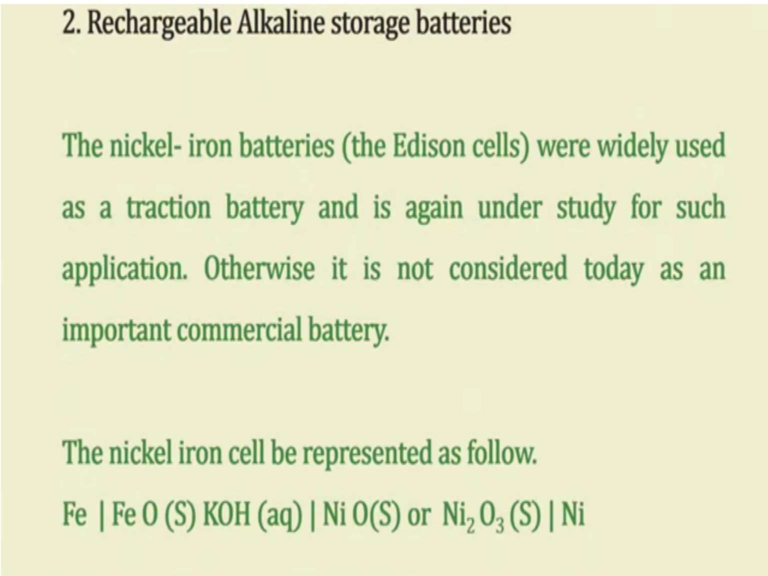

So, coming to rechargeable alkaline batteries what is there? These are known as Edison cells. They were widely used as a traction battery and is again under study for such applications otherwise it is not considered today as an important commercial battery nobody uses them nowadays nickel iron batteries.

But at one time lot of research was going on because nickel and iron both are abundantly available in the earth’s crust and lot of metal is being used. So, people thought that it could be a simple source for lot of energy in for the future unfortunately there are a number of operational problems one of them being both of them can corrode. One is nickel can react with sulfur in the air and nickel sulfate iron can get oxidized.

So, cathodic properties and anodic properties will keep on changing that is why they are not in favour for all kinds of applications. So, the nickel cell iron cell can be represented as follows. That is you have an iron electrode in contact with Fe O that is solid and that is mixed with KOH potassium hydroxide.

So, potassium hydroxide you cannot keep it solid, but it has to be in aqueous solution then the other electrode is Ni O that is the electrolyte or NI2 O 3 that is our solid and nickel is the cathode very simple reaction.

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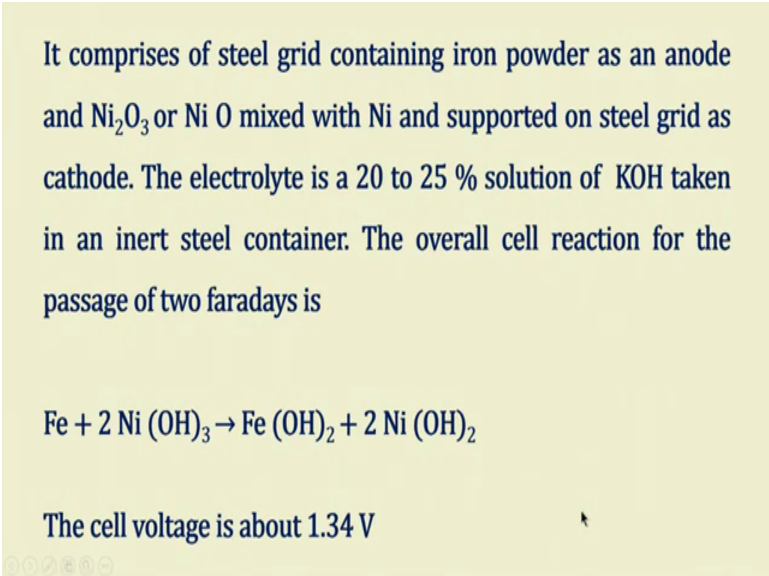


So, what you should do is you should have a steel grid containing iron powder as one anode. And Ni 2 O 3 or Ni O mixed with nickel as the second electrode.

So, steel grid as the cathode. So, the electrolyte is approximately 20 to 25 percent solution that is more than enough you can also work with 40 percent, 45, 50 percent solution of KOH. But that is not necessary it would not in any way help in getting the higher energy density nor the voltage nor the electron generation.

So, basically overall reaction will remain the same whatever is the concentration of the alkali. So, it because it is a 2 electron reaction again the passage of two faradays is required. And the chemical reaction can be represented as Fe plus plus 2 Ni OH 3 going to Fe OH twice plus 2 Ni OH twice where the nickel hydroxide and ferrous hydroxide ferrous hydroxide.

So, the cell voltage is approximately 1.34 volts. All these things I would if I ask you in the examination describe this nickel iron nickel battery or something like that you should be able to explain to me all these reactions in the examination. Basically what I would be asking is would it be correct stoichiometrically or not? Whatever what are the problems with the batteries? And why they are useful why they are not useful like that I have questions I will be asking.

So, please be go through all these slides carefully. And then I want you to study well for the examination also.

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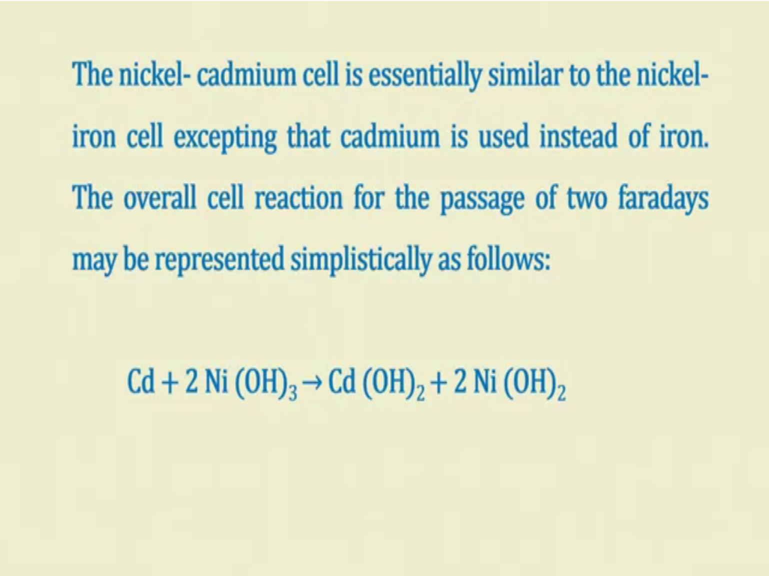


So, before I conclude today I would like to talk about nickel and nickel cadmium cell that is also essentially similar to nickel iron cell except that cadmium is used instead of iron. Why cadmium because cadmium is a much more reactive material than nickel. So, the overall cell reaction again for the same type of reaction two faradays is represented as cadmium and nickel hydroxide going to cadmium hydroxide and Ni OH twice.

So, what I would like to continue now, is give you some more information about some of the batteries what we have been using and where I want to conclude in the next class whatever we have been discussing about the batteries. So,

Thank you very much we will meet again.