

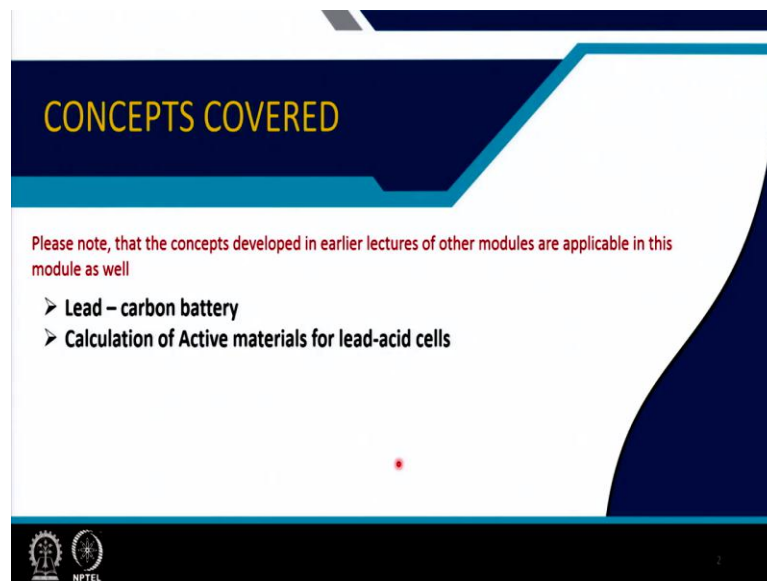
Electrochemical Energy Storage
Prof. Subhasish Basu Majumder
Department of Materials Science Centre
Indian Institute of Technology, Kharagpur

Module - 12
Other types of batteries
Lecture - 57

Lead Acid Batteries: Operational principles, main characteristics and applications
(Part - II)

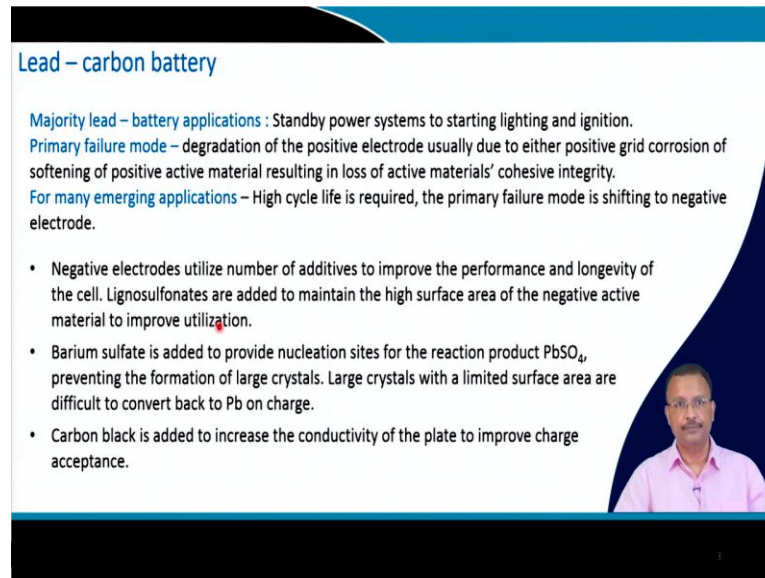
Welcome to my course Electrochemical Energy Storage. We are in the last module; module number 12 where I am very briefly describing Other types of batteries rechargeable batteries apart from those what already I have discussed in earlier modules. And this is lecture number 57 where I will continue this Lead Acid Battery, their Operational principle, main characteristics and applications.

(Refer Slide Time: 00:55)



So, here I will introduce the newly relatively new technology which is lead carbon battery. And then a brief calculation of the active materials what you use in lead acid battery as far as the active materials are concerned what are the ratios for a particular charge in order to get particular charge in the battery say 1 ampere hour how much material do you need. So, a brief illustration will be given in this particular lecture.

(Refer Slide Time: 01:32)



Lead - carbon battery

Majority lead - battery applications : Standby power systems to starting lighting and ignition.
Primary failure mode - degradation of the positive electrode usually due to either positive grid corrosion or softening of positive active material resulting in loss of active materials' cohesive integrity.
For many emerging applications - High cycle life is required, the primary failure mode is shifting to negative electrode.

- Negative electrodes utilize number of additives to improve the performance and longevity of the cell. Lignosulfonates are added to maintain the high surface area of the negative active material to improve utilization.
- Barium sulfate is added to provide nucleation sites for the reaction product $PbSO_4$, preventing the formation of large crystals. Large crystals with a limited surface area are difficult to convert back to Pb on charge.
- Carbon black is added to increase the conductivity of the plate to improve charge acceptance.

(A small video inset of a man in a pink shirt is visible in the bottom right corner of the slide.)

So, the major applications of lead acid battery is the standby power system and particularly this starting lighting and ignition that is used we call it SLI. So, this for the car system that lead acid still today it is using quite heavily and for standby power system for the UPS there are also lead acid batteries being used quite extensively till today.

So, the primary failure mode if you see that is the degradation of the positive electrode due to either positive grid corrosion you know that the grid material is important so that corrosion we will have to take care of it. And softening of this positive active material so, that is basically lead oxide that results a loss of the active material. So, you lose capacity.

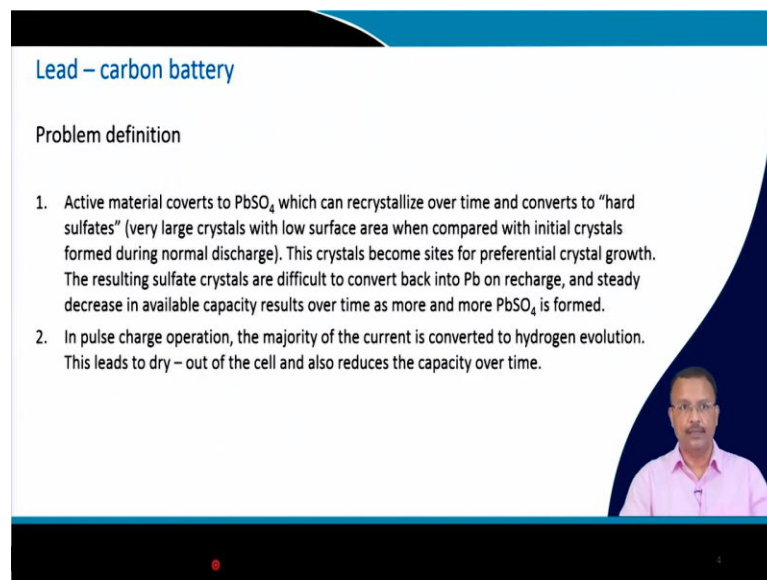
So, this integration of this positive electrode material to the grid that is important. So, for many emerging applications you need high cycle life. So, many times charge and discharge evaporation the cycleability is not that good for this kind of batteries. And primarily this was the failure mode which was related to the positive electrode but, now it is shifting to the negative electrode material as well.

So, negative electrode means lead. So, this negative electrode nowadays that utilizes number of additives to improve the performance and the longevity of the cell. So, a common additive is lignosulfonates they are added to maintain smaller particle size high

surface area of this negative active material and that is just to improve its utilization so, the capacity is improved.

And barium sulfate is one of the additives that is added to provide the nucleation site of lead sulfate and that basically prevents the large formation of lead sulfate because you know that again it will go back to lead. So, if this size of the crystal is very large with a very limited surface area it is difficult for them to convert back to lead on charge cycle. Apart from that carbon black is also added to increase the conductivity of the plate and the charge transfer resistance that is also reduced considerably once you add carbon black.

(Refer Slide Time: 04:22)



Lead - carbon battery

Problem definition

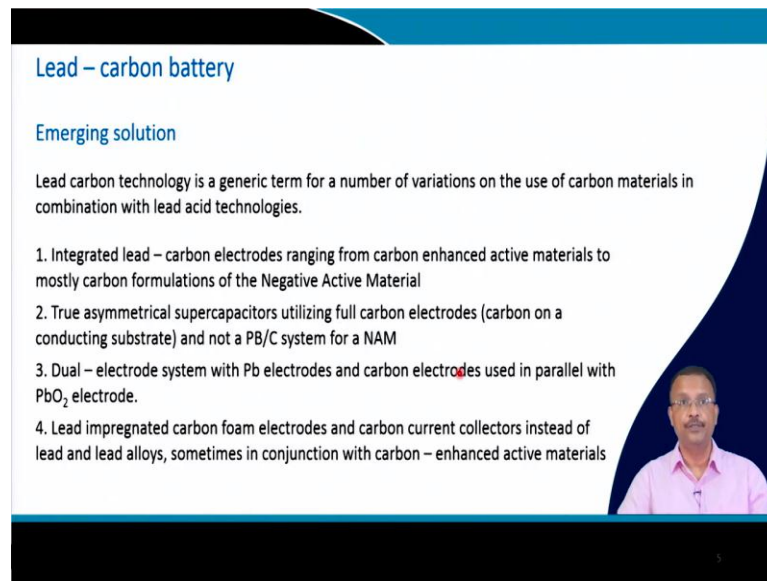
1. Active material converts to $PbSO_4$, which can recrystallize over time and converts to "hard sulfates" (very large crystals with low surface area when compared with initial crystals formed during normal discharge). These crystals become sites for preferential crystal growth. The resulting sulfate crystals are difficult to convert back into Pb on recharge, and steady decrease in available capacity results over time as more and more $PbSO_4$ is formed.
2. In pulse charge operation, the majority of the current is converted to hydrogen evolution. This leads to dry-out of the cell and also reduces the capacity over time.

So, if I define the problem of the lead acid battery that is first one is the active material converts to lead sulfate which can recrystallize over time of operation and then basically transfer into a hard sulfate. So, hard sulfate means very large crystals of lead sulfate which are having low surface area as compared to the initial nucleated lead sulfate

So, that of course, forms during the charge. So, for continuous operation this growth of this crystal that is one of the problems and this small crystal that basically grows to form a larger crystal and as I said it is difficult to convert it back to lead on recharge and therefore, this lead sulfate that becomes inactive and you lose the capacity over continuous period of operation.

So, the battery does not perform the way in the first day when it was used during discharge and charge. Particularly, if they are used for pulse charge operation so, the current that you are giving for charging the battery that basically converts water aqueous water to form hydrogen and it leads to hydrogen evolution. So, that water gets dissociated. So, that we call the dry out of the cell and this also reduces the capacity over the period of use. So, these are two major problems.

(Refer Slide Time: 06:22)



Lead - carbon battery

Emerging solution

Lead carbon technology is a generic term for a number of variations on the use of carbon materials in combination with lead acid technologies.

1. Integrated lead - carbon electrodes ranging from carbon enhanced active materials to mostly carbon formulations of the Negative Active Material
2. True asymmetrical supercapacitors utilizing full carbon electrodes (carbon on a conducting substrate) and not a Pb/C system for a NAM
3. Dual - electrode system with Pb electrodes and carbon electrodes used in parallel with PbO_2 electrode.
4. Lead impregnated carbon foam electrodes and carbon current collectors instead of lead and lead alloys, sometimes in conjunction with carbon - enhanced active materials

© 2014 Pearson Education, Inc. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/help/faq-fair-use/.

So, lead carbon technology that is basically an emerging I mean a generic term and this is one of the emerging solution for a number of variations on use of carbon material in combination with the lead acid technology. So, you are using this carbon material with this lead acid technology which is about 150 years old technology. So, there are different part I mean various way you can do that; the 1st one is integrated lead carbon electrode that range carbon enhanced active materials.

So, the carbon formulation in the negative active material with lead use carbon as well. So, that is integrating carbon in the negative electrode. Then a asymmetric super capacitor already I introduced a concept in my earlier lectures that utilize fully carbon electrode. So, carbon is basically pasted on a conducting substrate and it is not really a lead carbon system. So, this is B should be small case so, lead carbon system for a negative active material.

Then one can use a dual electrode system with lead electrodes and carbon electrodes that is used in parallel with the lead oxide. So, that is the 3rd category of lead carbon system. And 4th one is lead impregnated carbon foam electrodes and carbon current collectors instead of lead and lead alloys sometimes in conjunction with the carbon enhanced active materials. So, these are the four typical variation that you have in this emerging solution of the earlier problems to form lead carbon batteries.

(Refer Slide Time: 08:18)

Electrochemical equivalent weights of active materials in a lead-acid cell per Ah of electric charge (electricity)

Pb|PbSO₄ Electrode:
 The atomic weight of Pb is equal to 207.21 g. Two electrons of each Pb atom take part in the electrochemical reactions of charge or discharge in a lead-acid cell (LA cell). The equivalent weight of Pb, g_{eq}^{Pb} , is equal to:

$$g_{eq}^{Pb} = 207.21 / 2 = 103.61 \text{ g}$$

Let us determine the electrochemical equivalent weight of Pb per Ah. We will denote as δ_0 as the electrochemical equivalent weight per Ah of a given active material (δ_0^{Pb} ; $\delta_0^{PbO_2}$ or $\delta_0^{H_2SO_4}$).

$$\delta_0^{Pb} = 103.61 / 26.8 = 3.866 \text{ g Pb Ah}^{-1}$$

When 1Ah of electricity flows through the LA cell, 3.866 g Pb are oxidized at the negative plates during discharge or released during charge of a LA cell.

So, now let us see that how this to calculate this active material and it is quite straight forward first you will have to know the atomic weight of lead if you consider lead as a negative electrode material. So, that is about 207.21 gram. So, two electron of each lead atom is taking part in the electrochemical reaction in this system.

So, the equivalent weight which is defined as g equivalent for lead that is coming around 103.61 gram. So, this divided by 2. So, now you can determine the electrochemical equivalent weight of lead per ampere hour. So, we have denoted this symbol this delta 0 that is a electrochemical equivalent per ampere hour of a given active material. So, you have lead you have lead oxide and also you have H2SO4.

$$g_{eq}^{Pb} = 207.21 / 2 = 103.61 \text{ g}$$

So, in case of lead you have this equivalent weight 103.61 divided by this 26.8 you know that genesis of 26.8 from the Faraday law which already I have described earlier. So, this gives you about 3.866 gram of lead per ampere hour. So, 1 ampere hour electricity flows through the lead acid cell then basically 3.866 gram of lead is oxidized in the negative plate during discharge or released during charge.

$$\delta_0^{\text{Pb}} = 103.61/26.8 = 3.866 \text{ g Pb Ah}^{-1}$$

(Refer Slide Time: 10:05)

Electrochemical Equivalent Weights of Active Materials in a Lead-Acid Cell per Ah of Electric Charge (Electricity)

PbO₂|PbSO₄ Electrode

The molecular weight of PbO₂ is equal to 239.21g. Two electrons of each PbO₂ molecule take part in the electrochemical reactions of charge or discharge at the PbO₂|PbSO₄ electrode. The equivalent weight of PbO₂ is:
 $g_{\text{eq}}^{\text{PbO}_2} = 239.21 / 2 = 119.605 \text{ g}$

The electrochemical equivalent weight of PbO₂ per Ah is:

$\delta_0^{\text{PbO}_2} = 119.605/26.8 = 4.463 \text{ g PbO}_2 \text{ Ah}^{-1}$
 When 1Ah of electricity flows through the LA cell, 4.463 g PbO₂ are reduced to PbSO₄ at the positive plates during discharge or released during charge.

Similarly, you can calculate for lead oxide its molecular weight is 239.21, again two electrons are involved. So, you can calculate the equivalent weight 239.21 by 2. So, that is coming around 119.605 grams. So, electrochemical equivalent weight of lead oxide per ampere hour is you divide it by 26.8. So, that is coming around 4.463 grams of lead oxide per ampere hour.

$$g_{\text{eq}}^{\text{PbO}_2} = 239.21 / 2 = 119.605 \text{ g}$$

$$\delta_0^{\text{PbO}_2} = 119.605/26.8 = 4.463 \text{ g PbO}_2 \text{ Ah}^{-1}$$

So, when 1 ampere hour of electricity flows through the lead acid cell, then 4.463 grams of lead oxide are reduced to lead sulfate at the positive plate during discharge or release during charge.

(Refer Slide Time: 10:51)

Electrochemical Equivalent Weights of Active Materials in a Lead-Acid Cell per Ah of Electric Charge (Electricity)

H₂SO₄ Solution
 Sulfuric acid has a molecular weight of 98.08g and is divalent. Hence, its gram-equivalent weight is
 $g_{eq}^{H_2SO_4} = 98.08 / 2 = 49.04 \text{ g}$
 In the lead-acid cell, electrochemical reactions proceed at the two electrodes, which can be presented by the following general equation:
 $Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O$

2 g equivalents of H₂SO₄ take part in the above reaction, when 26.8Ah flow through the cell. The electrochemical equivalent weight of H₂SO₄ per Ah is:
 $\delta_0^{H_2SO_4} = 2 * 49.04 / 26.8 = 3.66 \text{ g H}_2\text{SO}_4 \text{ Ah}^{-1}$

When 1Ah of electricity flows through the cell, 3.66 g H₂SO₄ react at the two electrodes.

Similarly, for sulfuric acid this is the molecular weight and this gram equivalent weight is coming around 49.04 gram and in the lead acid cell the electrochemical reaction that proceeds at the two electrode which already you know that I have presented it by this reaction. So, 2 gram equivalent of H₂SO₄ that take part in this particular reaction, when basically 26.8 ampere hour flows through the cell. So, the electrochemical equivalent weight of H₂SO₄ this is coming into 2 into that 49.04 gram by 26.8.

$$g_{eq}^{H_2SO_4} = 98.08 / 2 = 49.04 \text{ g}$$

$$\delta_0^{H_2SO_4} = 2 * 49.04 / 26.8 = 3.66 \text{ g H}_2\text{SO}_4 \text{ Ah}^{-1}$$

This is coming around 3.66 gram of H₂SO₄ ampere hour. So, 1 ampere hour electricity flows through the cell then 3.66 grams of H₂SO₄ that reacts with the two electrode system.

(Refer Slide Time: 11:57)

Electrochemical Equivalent Weights of Active Materials in a Lead-Acid Cell per Ah of Electric Charge (Electricity)

The proportion by weight of active materials in a lead-acid cell that take part in the electrochemical reactions during cell operation is:
 $\text{Pb} : \text{PbO}_2 : 2\text{H}_2\text{SO}_4 = 207.21 : 239.21 : 2 * 98.08$

The weights of PbO_2 and H_2SO_4 vs. the weight of Pb give:
 $\text{PbO}_2 : \text{Pb} = 1.154$
 $\text{H}_2\text{SO}_4 : \text{Pb} = 0.947$

So the proportion by weight of the active materials (NAM : PAM : H_2SO_4) that take part in the charge or discharge reactions, when electricity flows through a LA cell, is:
 $\text{NAM} : \text{PAM} : \text{H}_2\text{SO}_4 = 1.00 : 1.154 : 0.947$

So, the in proportion by weight the active material in lead acid cell take part in this electrochemical reactions. So, lead is to lead oxide is to twice H₂SO₄ that is coming around these values. So, weight of lead oxide and H₂SO₄ versus weight of the lead that gives lead oxide is to lead is 1.154 from the calculation and H₂SO₄ is to lead is 0.947.

So, the proportion weight of this negative active material is to positive active material is to H₂SO₄ that you can determine as 1 is to 1.154 is to 0.947. So, that is a basic calculation that you can do to understand that to get 1 ampere of charge how much active electrode that you do need.

$$\text{NAM} : \text{PAM} : \text{H}_2\text{SO}_4 = 1.00 : 1.154 : 0.947$$

(Refer Slide Time: 12:57)



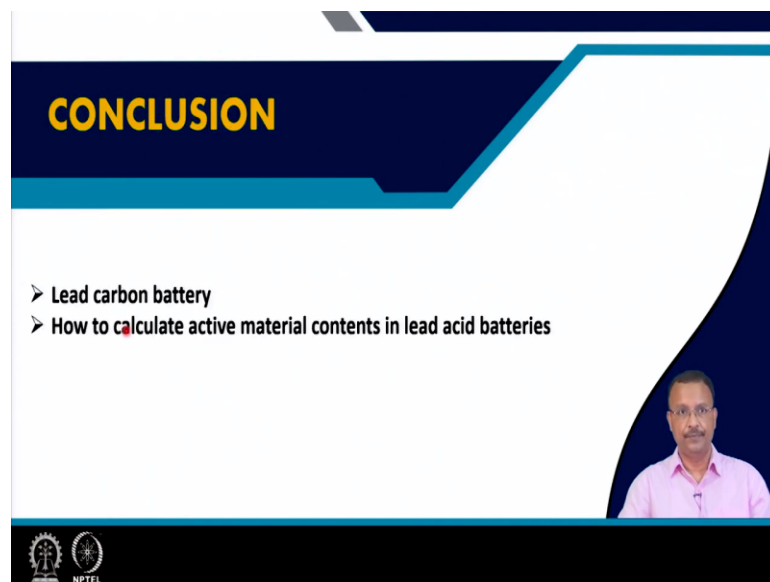
REFERENCES

- **Pei Kang Shen et al** *Electrochemical Energy : Advanced Materials and Technologies*, Chapter 10 Advanced Technologies for lead – acid rechargeable batteries page 219 CRC Press (2016) (Study material)
- **Detchko Pavlov**, *Lead-Acid Batteries Science and Technology*, Elsevier Publishing House

NPTEL

So, there is a good book on Lead Acid Battery by Pavlov and for the other part the book by Advanced by this Shen it is a edited volume chapter 10 and that you can use as your study material.

(Refer Slide Time: 13:20)



CONCLUSION

- Lead carbon battery
- How to calculate active material contents in lead acid batteries

NPTEL

So, in this particular lecture we talked about lead carbon battery which is basically introduced to overcome the problems associated with VLA and VRLA type of lead acid batteries. And then a basic calculation to show the active material contents how to calculate that in a lead acid batteries.

Thank you for your attention.