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Studying the Effect of H_2SO_4/H_2O Ratio on the Properties of Positive Electrode in Lead-acid Battery

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Abstract

The lead-acid battery has become so dependable in its used applications of automobile starting, emergency lighting and telecommunications, which left an impression that no further investigation is necessary or desirable.

While there has been slow continuous improvements in lead-acid battery performance and mainly limited to design and material engineering.

This work is mainly devoted to the properties of the active mass of the positive electrode and the acid/water ratio during the manufacturing process.

A field study is carried out at the State Battery Manufacturing Company located in Baghdad, to prepare batches of lead mono-oxide with predefined quantities of liquid additives (i.e. sulfuric acid and water).

Quality control and laboratory routine analysis using X-ray diffraction, porosimeter and BET techniques, as well as density, penetration tests of residual lead content ware conducted during the batch process.

After the assembling of the positive plates produced during this research into the final product, final testing including electrical capacity and dry charging were performed.

It was concluded from the results obtained, that the effective H_2SO_4/H_2O ratio and hence H_2SO_4/PbO ration and paste density with α/β-PbO_2, are the limiting factors of the electrical capacity and durability of the batteries concerned.

***Keywords*:** lead-acid battery, positive electrode.

Introduction

The manufacture of secondary batteries based on aqueous electrolyte forms a major part of the electrochemical industry. By far the largest total capacity produced is that of lead-acid batteries whose dominance is due to a combination of low cost, versatility and the excellent reversibility of the electrochemical system. The lead-acid batteries have extensive use both as portable power sources for vehicle service and traction, and in stationary applications ranging from small emergency supplies to load leveling systems [1].

A typical lead-acid battery consisted of three active elements, namely; positive plate, negative plate and diluted sulfuric acid. In State Battery Manufacturing Company (S.B.M.C.) many types of lead-acid battery are produced, but all of these are classified as starting, lighting & ignition (SLI) batteries (Which is a battery of usually 12 volts or 24 Volts used for starting, lighting and ignition in vehicles with internal combustion engines).

In SLI Battery, the dominant element in design calculations and material balance is the positive plate [2,3]. So, the improvements in positive plate characteristics will lead to increase in the battery efficiency and life. The positive plates are prepared by progressive production stages. But, it is reported that the mixing process defines the major characteristics of the final battery.

The principles of mixing process is to provide a porous mass with sufficient porosity to give the coefficient of requirement performance for the formed active mass and adequate rigidity and cohesion to withstand vibration in service, as well as the dimensional changes involved in each discharge-charge cycle, for the specified life time of battery. Water is used as pore-forming agent and sulfuric acid is added to provide the basic sulfates, which cause the necessary cementation [3].

The main parameters related to paste mixing process are listed as follows:

- Temperature of Mixing Process.
- H_2O/PbO Ratio.
- H_2SO_4/PbO Ratio.
- pH

The electrical capacity of positive plate is controlled by the inner and outer parameters [7], which are listed in table 1.

Table 1, The inner and outer parameters controlling the electrical capacity of positive plate

Inner parameters	Outer parameters
• Chemical composition • Crystal morphology • Porosity • Pore distribution • Inner surface area • Conductivity • Impedance • Inhibitors • Double layer adsorption	• Current density • Temperature • Acid concentration • Plate thickness

It was reported that [3,6,7]:

- In general, the effects of inner parameters are higher than the outer parameters.
- Above parameters are dependent of one another, and should be considered together.
- Regarding the ratio α-PbO2/β-PbO2, It has been found that the best ratio is equals to 0.8 for the purpose of SLI batteries [8].

The aim of the research is to determine relationships between H_2SO_4/PbO ratio and paste density with α/β-PbO_2 ratio. So, controlling the electric capacity and life time of battery by varying these parameters

Experimental Work

The positive plates of SLI lead-acid batteries are manufactured according to a time-honored industrial process in which a mixture of finely divided lead, lead oxide, basic lead sulfates, water and sulfuric acid is pressed, in the form of a paste, into a grid of a lead alloy. The pasted grids are held in an environment of controlled humidity and temperature for re-crystallization process. The plates are then electrochemically formed in a dilute sulfuric acid electrolyte to convert the active material to PbO_2. The forming process involves a complicated sequence of reactions, and it is necessary to carry out the formation in two stages separated by a hold time in order for most of the active mass to be converted. The details of manufacturing process may vary from one manufacturer to another, but the whole operation, which is performed on batches of plates, usually takes about a one week.

In the present study, eight experiments were conducted in Babil-1 Factory\S.B.M.C. for producing positive plates of different mixture ingredients. Each one carried out according to the outlines illustrated in Fig. 1.

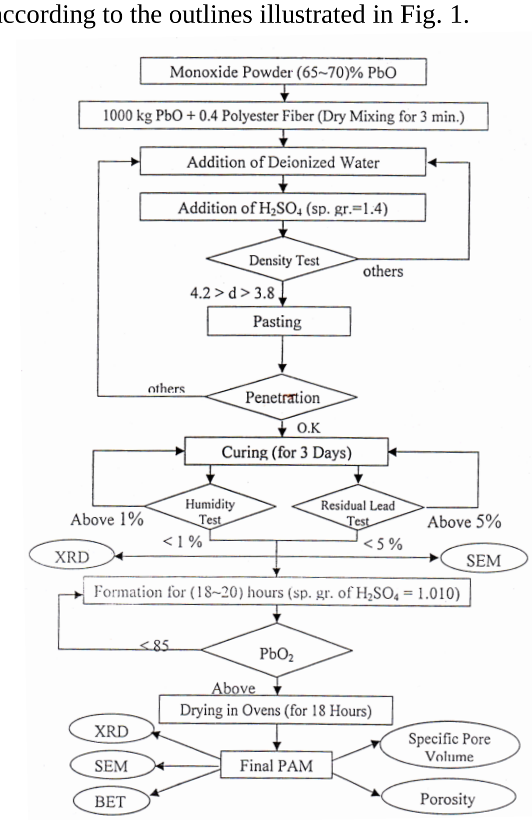

Fig. 1 Lists the experimental data for the eight conducted experiments

Table 2 The experimental data of present work for 1000 kg lead oxide, 0.4 kg fiber additives, 6 lit/min acid and 10 lit/ min water additive rate

Run No.	Sulfuric acid, liter	Deionized water, liter	H2SO4/PbO, wt. ratio	Paste density, g/cm^3
1	61.0	140	8.5	4.10
2	76.0	140	10.6	4.10
3	82.0	140	11.5	4.10
4	86.0	140	12.0	4.10
5	96.5	140	13.5	4.10
6	82.0	135	11.5	3.85
7	82.0	160	11.5	4.10
8	82.0	175	11.5	4.50

Analysis and Testing

Chemical Tests

The chemical tests were conducted according to the testing standards of Chloride Technical Limited.

Lead monoxide Content

Lead Dioxide Content

Physical Tests

PAM Apparent Density Determination

This test was conducted using mercury porosirneter of RUSKA Brand, the apparent density (DA) was calculated as follows:

$$D_A = \frac{W_l - W_g}{V_l - V_g} = \frac{\text{Active Material Weight}}{\text{Active Material Volume}} \quad (1)$$

Where:

W_l is weight of the sample,

W_g is weight of the grid,

V_l is volume of the sample,

V_g is volume of the grid.

Paste Density Test

T1- is carried it using a special cup supplied with the paste mixer by the manufacturer to determine the paste density [7].

Surface Area Measurement (BET Test)

The internal surface area for the samples of PAM was determined using BET method. The testing apparatus is ASAP 2400, Brand; Micromeritics Instrument. This method is based on the measuring of nitrogen gas adsorbed as result of pressure decrease due to adsorption of a dose of known volume of the gas.

X-Ray Diffraction Test (XRD)

The XRD tests were conducted using a diffractometer of SIEMENS brand, model; SRS D-500, Its specifications are; Tube; Cu, Voltage; 40 KV, Current; 20 mA, Wave Length; 1.5050 A°, 22θθθθθθ 0 range is 20° to-60°.

Scanning Electronic Microscopy Investigations

A Canibride Brand SEM instrument, Type; Stereoscan 240, Magnification; 100,000 was used for examining samples of cured and formed pastes before starting this test.

Electrical Tests

For each experimental run, two batteries were assembled using positive plates made from the obtained paste. These batteries were tested according to the international electrochemical commission standard (IEC-95) to examine the electrical specifications [9]. Two tests were conducted, namely; Electrical capacity test and dry charging test.

Results and Discussion

Effect of H_2SO_4/PbO Ratio on α/β-PbO Ratio

The formed plates contain both the acidic β and alkaline α polymorphs of PbO_2. The capacity and life of battery is determined by the ratio of a β- PbO_2.

The relationship between the ratios α/β-PbO_2 and H_2S0_4/PbO is illustrated in Fig. 2, which demonstrates that a decrease in H_2S0_4/PbO ratio involves an increase in α/β-PbO_2 ratio. This behavior is existed because in high sulfatized paste (of 12 to 13 H_2S0_4/PbO ratios) the paste maintains a low pH value on the reaction layer during the formation process, which leads to the dissolution precipitation-mechanism and forming a large amount of β-PbO_2.

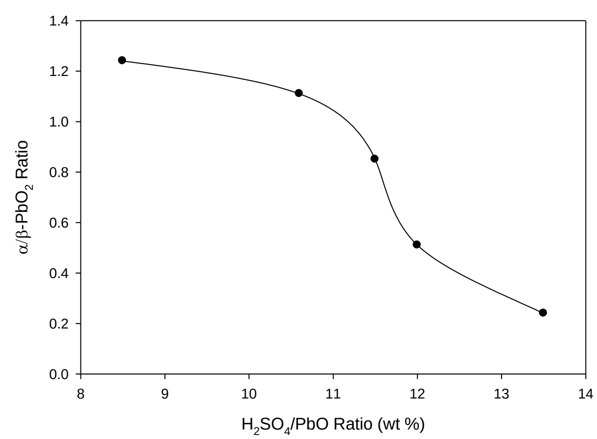

Fig. 2 The relation between H_2S0_4/PbO and α/β-PbO_2 ratio

Effect of H_2O/H_2SO_4 Ratio on the Paste Density

The increase of PAM density decreases the movements of electrolyte sulfate ions during formation process and maintains the interior of the plate alkaline for a longer time. So, the α-PbO_2 polymorph will be of high content resulting in the increasing of α/β- PbO_2 Ratio, as shown in Fig. 3.

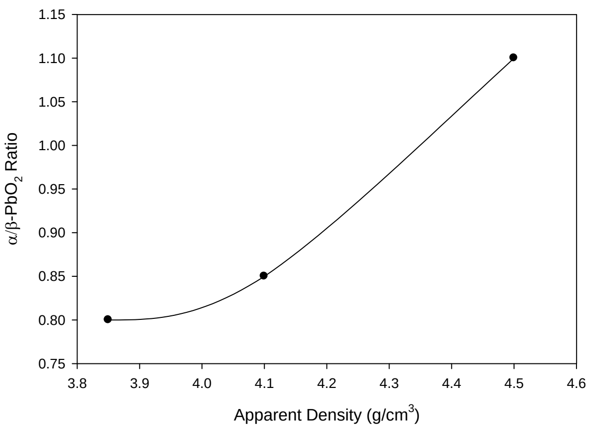

Fig. 3, The relation between α/β-PbO_2 ratio and apparent density

Effect of H_2S0_4/PbO Ratio on the Internal Surface Area of PAM (BET)

The internal surface area increases with increasing H_2S0_4/PbO ratio and that is because the increasing in H_2S0_4/PbO ratio will produce a rise in the value of specific pore volume leading to increase the number of pores occupying the same pore volume and that results in a high surface area. As shown in Fig. 4.

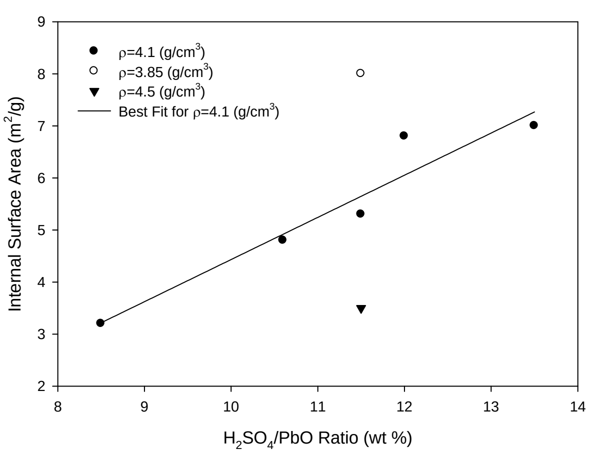

Fig. 4, Effect of H_2S0_4/PbO Ratio and Density on the Internal Surface Area

Also, Fig. 4 demonstrates that the apparent density of PAM exerts au exceptionally strong influence on the internal surface area.

Effect of H_2SO_4/PbO Ratio on the Electric Capacity

The electric capacity is characterized by all discussed parameters. The structure of PAM considers as a limiting factor for the obtained capacity and it is controlled through the varying of specific pores volume and in a smaller degree by internal surface area. The first parameter determines the fluxes of ions taking part in the reaction, while the latter parameter indicates the surface area that the electrochemical reaction can take places upon it. Fig. 5 shows that an increase of the H_2S0_4/PbO ratio will lead to increase of the battery electric capacity.

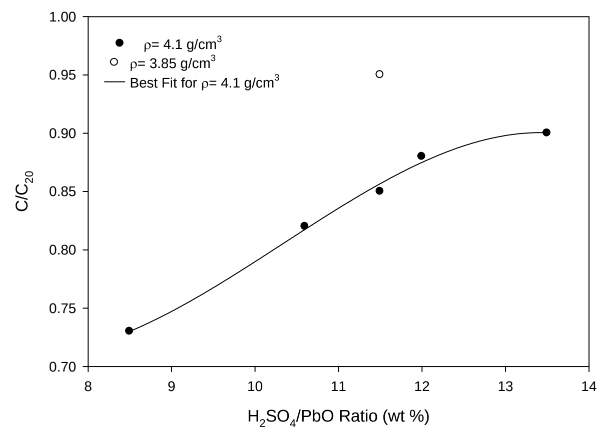

Fig. 5, Effect of H_2S0_4/PbO Ratio on Electric Capacity

Conclusions

From the present work, the following conclusions can be obtained:

1. The effect of decreasing apparent density of PAM exerts a strong increasing of the internal surface area and accordingly increasing the obtained electric capacity of the complete battery.
2. The adding rate of water and sulfuric acid are important parameters during the mixing process of positive paste since they are controlling the working temperature and paste density.
3. It was found that the best ratio of cx/13-Pb02 for SLI battery (which is equal to 0.8 f83 can be almost obtained by using the following mixing parameters:
   - H_2SO_4/PbO = 11.5 %
   - ρ= 3.85 g/cm^3

   These values give α/β-PbO_2 = 0.79 (from XRD Analysis).

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