SOME ELECTROCHEMICAL STUDIES
ON THE BEHAVIOUR OF
LEAD ELECTRODES

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CHAPTER I
INTRODUCTION

A:Electrodes of Lead-Acid Cells

1-Historical Development and Construction

The storage battery of today grew out of the investigations of many early experiments in the field of electrochemistry. Volta's[1] discovery of the galvanic battery in 1800 initiated this line of research. Since then several experiments entered the field, but it remained for Planté[2], 1859, to develop a valuable form of cell as a result of his study of the properties of metals for the accumulation of oxygen. The cell consisted of two sheets of lead separated by strips of rubber and rolled into the form of a spiral. The element thus formed was immersed in a dilute solution, about 10 per cent of sulphuric acid.

The formation of the active material on the Planté-plates required considerable time and the expenditure of a large amount of electrical energy. In 1881 Fauré[3] patented a process for pasting the surface of the plates with a compound of lead which could be formed more easily into the active material of the finished battery, but the adherence of the active material to the plates was rather poor. Volckmar[4] patented the use of lead plates with numerous holes which were filled with a paste made of pulverized lead mixed with sulphuric acid. Swan[5] also obtained a patent on a grid of cellular structure. These supports for the active material were an improvement over the flat plates which Fauré used, but the active material still fell out readily. Sellon[6] patented a modification of the grid to make it held the active material. The cellular structure in his grid was designed in two planes so as to lock the active material between them. Sellon was also the first who used lead-antimony alloy for his grid.

The essential difference between Planté-plates and pasted-plates consists in the fact that the active materials of the former are derived from the body of the plate itself, whereas for the latter they are formed from oxides or other pastes applied to the plate mechanically. Planté-plates serve quite a different purpose from the pasted plates. They are ordinarily much larger and heavier than the pasted plates and have a relatively smaller capacity. They are suitable for stationary batteries, in which considerations of space and weight are of less importance than durability. The underlying lead constitutes the essential weight of the Planté-plate.

The grids in battery-plates have to serve several purposes, namely:

1. They must be mechanically stable to retain the active pastes as securely as possible.
2. The grid must be able to distribute heavy current uniformly without undue drop of potential which may be caused by either too small a cross section of the grid bars or by too small a contact area between the grid metal and the active paste.
3. On the other hand, local actions at the contact area PbO_2/Pb cause loss of charge during standing of the cell. Thus, grids for batteries which are intended to have good "retention of charge" should be constructed in a way that these contact areas are comparatively small.
4. The grid-alloy must be as resistant as possible against electrochemical oxidation. The molten alloy must flow easily and completely through all the channels of the casting moulds, at moderate temperatures.
5. The solubility of alloy-components more noble than lead, such as antimony, should be as small as possible.
6. During service time, grids should as small as possible grow or tend to bulge, as a result of corrosion.

All requirements, [illegible] by one construction or one alloy alone, as some of them are contradictory. Engine-starting batteries, for instance, which have to produce very high current for short time and meanwhile possess maximum capacity per weight, should contain very thin plates. The grids need an alloy which will readily flow through the thin channels of the mould, has a good resistivity against electrochemical oxidation, and gives grids of high mechanical strength. Traction batteries, however, which are deeply discharged during service, need grids which are much more robust and give a safe paste-retention to avoid early shedding. For this type of battery, the active paste is enclosed in synthetic porous tubes. Batteries which must have a high charge retention, need grids with mainly the properties as given above sub (3) and (5). Approximately the same applies for stationary batteries which should have a service life of more than 10 years. Such batteries need grids made from pure lead, lead-calcium alloy, or dispersion hardened lead.

Pure lead grids are not rigid enough, and casting of thin grids from pure lead is difficult. Therefore, most grids are made of lead alloyed with about 6 per cent antimony. The antimony is well known to affect cell behaviour in several ways, but the benefits resulting from its use have outweight its deletrious effects, and today only special purpose cells are manufactured without antimony. The antimonial alloys are easier to cast and the strength of the alloy makes it possible to handle the thin grids. The expansion coefficient of the alloy is less than that of pure lead. In addition, antimony minimizes grid growth by distributing corrosion attack across the body of the grains, relieving attack at the grain boundaries. Besides, it has been recently observed that the antimonial cells can maintain their capacity by keeping the active material firm during service. However, antimony goes into solution by anodic corrosion and deposits on the negative plate. The hydrogen overvoltage on antimony is lower than on lead, and this causes spontaneous self-discharge of the negative plate. The efficiency of charge also decreases as increasing portions of the charging current are wasted on generation of hydrogen.

The pastes now commonly used in making the familiar pasted-plates are prepared by mixing some particular lead oxide with a dilute solution of sulphuric acid. Reactions occur that result in the formation of basic lead sulphate. The lead sulphate is the cementing material which makes a firm plate. The lead sulphate also expands the paste. Too little expansion results in hard, dense plates and needless limitation of the ampere-hour capacity of the plate. On the other hand, too great expansion may result in shedding of the active material and thereby shorten the useful life of the battery[7].

After curing, the positive and negative plates are electrolytically oxidized and reduced in dilute sulphuric acid. The word "Formation" applies primarily to the process adopted by Planté to create a layer of sponge lead on the surface of the negative plates and of lead dioxide on the positives to constitute the active materials of the cell. The "Formation" of pasted plates, on the other hand, means the oxidation or reduction of the lead oxides or other materials which have been applied to the grids.

A-The Double-Sulphate Theory

The double-sulphate theory was given, in 1882, by Gladstone and Tribe[8]. They discovered by analytical studies that lead sulphate was formed at both plates during discharge. They suggested that the cell reaction is:

$$Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O$$

From left to right this equation represents discharge, and from right to left charge.

Other views were proposed for the chemistry of the lead-acid cell. Thus Baur and Glaessner[9] postulated the existance of a higher oxide of lead, PbO_3. Glasstone[10] attributed the evolution of oxygen at the lead dioxide electrodes to the intermediate formation of an unstable higher oxide. According to Fery[11], the charged positive plate contains a higher oxide of lead, possibly Pb_2O_5, which during discharge is reduced to PbO_2, not to $PbSO_4$. At the negative plate, he assumed during the discharge, the formation of Pb_2SO_4, a substance which readily oxidizes in air to $PbSO_4$. Riesenfeld and Sass[12] claimed to have established, by X-ray analysis, that basic sulphate of lead is formed on the discharged positive plate.

However, Macinnes and co-workers[13] showed that chemically prepared lead dioxide has the same chemical composition and yields the same potential in sulphuric acid as the active material of the positive plate. Mazza[14] and Barrett[15] identified PbO_2 and $PbSO_4$ in the plates by the use of X-ray with no indication of conflicting substances. Other investigators comprising Gérard[16], Kinosita[17], Denina and Ferrero[18], Denina and Fornaseri[19], Sinn[20], Cohen and Overdijkink[21], onfirmed the "double-sulphate theory". Vinal and Craig[22], found that two equivalents of sulphuric acid are consumed per faraday and that two equivalents of water are formed at the same time. They also found no evidence for the formation of basic sulphate, and no spontaneous change in the final products of the reaction was observed after the discharge process was discontinued.

Later Beck and Wynne-Jones[23] concluded from thermodynamic studies of published information on the effects of variations of temperature, pressure and concentration of the electrolyte, that the data are consistent only with the "double-sulphate theory".

3-Reactions at the Negative Plate

Although the "double-sulphate theory" states that lead sulphate is formed at each plate during discharge, and is converted during charge into lead at the the negative plate, and lead dioxide at the positive plate, it does not explain the actual processes occurring at the negative and positive plates.

However, at the negative plate the process is relatively simple. The lead ions produced during discharge react with the sulphate ions forming lead sulphate. According to Kabanov, Leikis and Krepakova[24], the thickness of the lead sulphate layer increases with decreasing current density and increasing temperature. Fleischmann and Thirsk[25] stated that the number of lead sulphate crystals in the deposit decreases while their size increases with decreasing overvoltage.

Vaisberg, Krivolapova and Kabanov[26] found that increasing the concentration of sulphuric acid results in a decrease of the time necessary for the anodic oxidation of a lead surface to lead sulphate. Lorenz[27] by anodic impulse measurements, proved that