

ON THE HISTORICAL DEVELOPMENT OF THE LEAD/ACID BATTERY, ESPECIALLY IN EUROPE

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Introduction

The lead/acid battery is more than 100 years old. Nevertheless, only a few publications [1 - 3] have dealt with the history of this system. Up to 1880, the lead/acid battery was of little importance. But with the technical revolution of that time, the role of the battery increased notably. Many inventions contributed to improvements in the performance of the battery [4 - 9]. Three patents were registered in Germany up to 1881, whereas 69 and 82 patents were registered for the periods 1881 - 1885 and 1885 - 1890, respectively. Most of these developments have been forgotten, but some of the principles are in use today.

Discovery of the lead/acid accumulator

Johann Wilhelm Ritter (1776 - 1810) (Fig. 1) discovered the first accumulator system in 1801. The so-called 'RITTERsche Säule' consisted of copper plates separated by NaCl-impregnated sheets of paper, *i.e.*, Cu/H₂O, NaCl/CuO. The charging voltage was 1.3 V and the discharge voltage was 0.3 V. Ritter also experimented with lead, tin, and zinc electrodes, but did not use a sulphuric acid electrolyte. Thus, the lead/acid system was found 50 years



Fig. 1. Johann Wilhelm Ritter (16.12.1776 - 23.1.1810) [3].



Fig. 2. Wilhelm Joseph Sinsteden (6.5.1803 - 11.11.1891) [3].

later, although in the meantime PbO_2 was produced in an electrochemical way by Kästner (about 1810) [10], Nobili (1828) [11], Schönbein (1838) [12], de la Rive (1843) [13], and Wheatstone (1843) [14].

Wilhelm Joseph Sinsteden (1803 - 1891) was a German medical officer (Fig. 2). In addition to his medical work in an army regiment in Pasewalk, he also found time to investigate electrical phenomena, *e.g.*, a.c. motors. In connection with those studies, Sinsteden used several electrochemical cells in order to measure the current. In one cell, electrodes were made from lead, and dilute H_2SO_4 was used as the electrolyte. Sinsteden perceived the electrical storage capability of this system and thus discovered the working principle of the lead/acid system. From results published in 1854 [15], the energy density of this complete accumulator can be calculated to be lower than 0.1 W h kg^{-1} at the 15-min rate.



Fig. 3. Gaston Planté (22.4.1834 - 22.5.1889) [3].

Gaston Planté (1834 - 22.5.1889) (Fig. 3) was a French scientist who dealt with an unusual variety of topics including palaeontological, theological, and electrical problems. In his electrical work, Planté used voltameters and discovered the operating principles of the lead/acid system independently of Sinsteden in 1859 [16]. Planté, however, more clearly recognized the practical importance of this discovery and started to construct technical cells (rolled, prismatic) and accumulators [16].

Charles Kirchoff developed a solution accumulator with platinum electrodes in a $\text{Pb}(\text{NO}_3)_2/\text{Pb}(\text{CH}_3\text{COO})_2$ electrolyte in New York in 1861 [17]. Finally, Wilhelm Siemens also discovered the lead/acid system about 1860. He used active coal impregnated with lead salt [18].

Theory of the lead/acid accumulator

The first theory of the lead/acid system was published by Gladstone and Tribe in 1882 [19]. These authors stated that the following reactions occur:

negative electrode:



positive electrode:



It should be noted that PbO was proposed as a discharge product of the positive electrode. The self-discharge (local action) reaction was also discussed. The theory of the lead/acid system was also examined in detail by Aron in 1883 [20]. In particular, the relation between specific density and discharge time was established and a description was given of the sulfation phenomenon. Frankland proposed basic sulfates ($5\text{PbO} \cdot 3\text{SO}_3$) as discharge products in 1890 [21]. Dolezalek gave a detailed description of the theory in his book *Die Theorie des Bleiakкумуляtors* [22].

Development of the lead/acid accumulator

Fauré covered lead plates with porous active mass in 1881 [23]. This mass was protected by sheets of cloth or felt. His lead/acid cell had a specific energy of 8 W h kg^{-1} at the 10-h rate. Brush, an American scientist, used the same idea for his accumulators.

Grids were invented by Volckmar in Paris in 1881 [24]. Thus, the pasted electrode was created but did not find widespread application until the middle of this century. This was brought about by the development of new separators that increased the service life of the electrodes.

Tudor [25] improved Volckmar's plate in 1886 by using plates with conical ribs. The latter were pre-formed electrochemically and then pasted with active mass. This type of electrode is still in use today.

In 1883, Philippart [26] produced electrodes by cylindrically wrapping a lead spin with active mass. At that time, the active mass was protected by ebonite rings. Later, Woodward used rubber pipes for this purpose; such electrodes are well known today as iron-clad electrodes.

Holder for active mass

Fabraky and Schenek [27] submitted a patent in 1880 for grids with circular segments in order to avoid the buckling of plates (Fig. 4). The areas 'B' in the grid were not pasted and were intended to relieve any strain imposed upon the electrode by expansion of the active material. The Bell Company has used the same idea in its circular design of grid.

In 1885, the Primary Battery Company Limited invented [28] a combination of a conducting grid with collector action and an insulating grid (hard rubber) with a mechanical function. The conducting grid was partially embedded in the insulator. The aim was to reduce the mass of the active mass holder. Pepper [29] in 1890 used radial grids that were cast directly into the active mass (Fig. 5). This type of grid is now used by several companies.

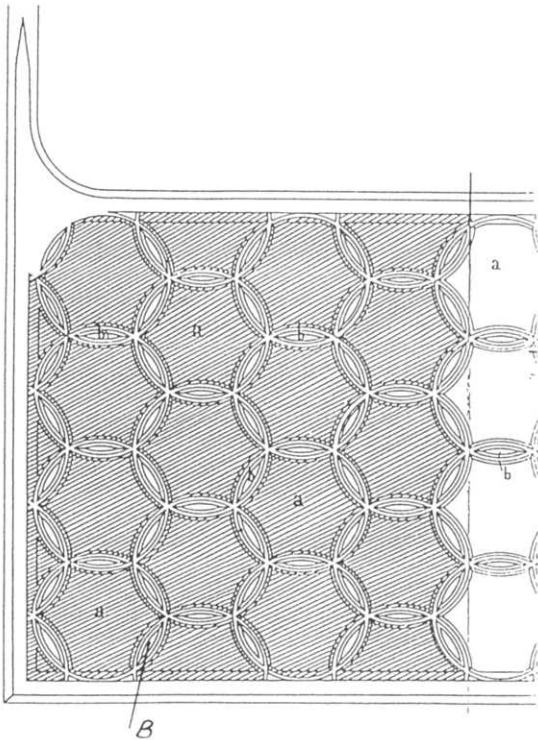


Fig. 4. Grid developed by Fabraky and Schenek [27].

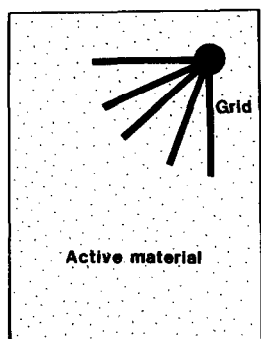


Fig. 5. Radial grid in the Pepper electrode.

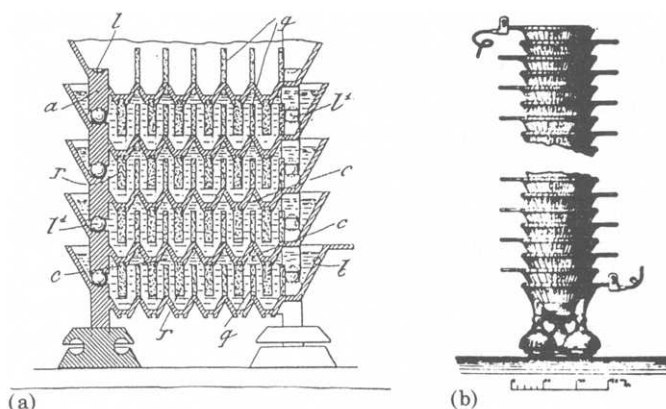


Fig. 6. Accumulator of Tribelhorn [31].

In 1888, Gestel [30] introduced a copper grid that was covered with lead by either pressing or melting. Today, such grids are produced in the F.R.G. by Hagen Batterie AG. Tribelhorn [31] produced a bipolar accumulator in 1897; the electrodes were separated by glass balls (Fig. 6). Neving [32] proposed, in 1890, the use of a lead-tin alloy as a grid material. Bandsept [33] in 1890 produced electrodes for a Planté-type accumulator by pressing lead dust.

Active mass

Aron [34] used cellulose as an additive to the active material in 1882. It was claimed that the electrolyte could penetrate more deeply into the active mass. This notion still applies today since carboxymethyl cellulose is added to positive plates.

Müller in 1882 [35] and Gardner in 1886 [36] filed patents describing the use of carbon additives to the active mass in order to increase the conductivity. Today, carbon, especially soot, is also used as an additive.

In 1884, Kalischer [37] produced active mass with mercury in order to avoid the growth of dendrites.

Electrolyte

Zierfuss [38] in 1888 and Schoop [39] in 1890 proposed a gelled electrolyte, consisting of SiO_2 and H_2SO_4 , to produce leak-proof accumulators. Present sealed batteries employ such an electrolyte.

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