

## The Gaston Planté Medal Address

Paul Ruetschi

Leclanché SA, 1400 Yverdon-les-Bains (Switzerland)

Mr Secretary General of the Bulgarian Academy of Sciences, Professor Budevski, Professor Pavlov, Ladies and Gentlemen:

I feel greatly honoured that the International Planté Medal Committee has deemed my work to be worthy of this award. May I express my warmest thanks to the Committee. If my contributions have been of use in advancing the science and technology of lead/acid batteries, I am already more than rewarded.

Over the years, I have had the help of a number of coworkers whose contributions I would like to acknowledge here. Let me mention the names of the following coauthors: R.T. Angstadt, R.F. Amlie, B.D. Cahan, R. Giovanoli, J.B. Ockerman, J. Sklarchuk and J.C. Venuto. Finally, I would also like to acknowledge the support I have had from the two Companies that I have worked for, namely, The Electric Storage Battery Co. in the USA, and Leclanché SA in Switzerland.

My first contacts with the science and technology of lead/acid batteries go back 40 years. I was then still at the Federal Institute of Technology in Zurich. A couple of businessmen had approached me to look into new ways of making a lead/acid battery. Together with my brother, I designed and built a battery based on the Planté process [1]. The plates were fabricated from thin lead foils, and had a thickness of less than 1 mm (Figs. 1, 2). Current collectors were resistance-welded to the foil-plates, and a grid pattern, or a pattern of small dots of acid-resistant lacquer, was sprayed or painted on to the plates in order to mask that part of the surface that was to be protected from anodic attack. The plates were formed anodically in dilute acid that contained nitrate. The negatives were washed and impregnated with an expander suspension, prior to reducing the  $PbO_2$  layer to sponge lead. Needless to

April 21, 1959

K. RUETSCHI ET AL

2,883,443

LEAD-ACID STORAGE BATTERY

Filed July 13, 1956

2 Sheets-Sheet 1

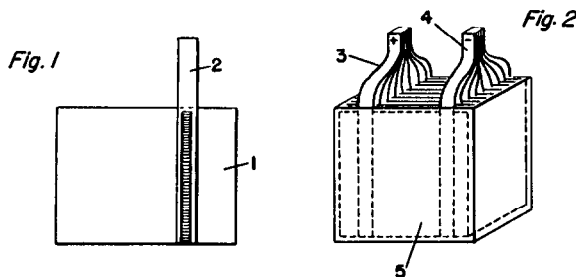


Fig. 1. Design of lead/acid battery as proposed by K. Ruetschi and P. Ruetschi [1].

April 21, 1959

K. RUETSCHI ET AL  
LEAD-ACID STORAGE BATTERY

2,883,443

Filed July 13, 1956

2 Sheets-Sheet 2

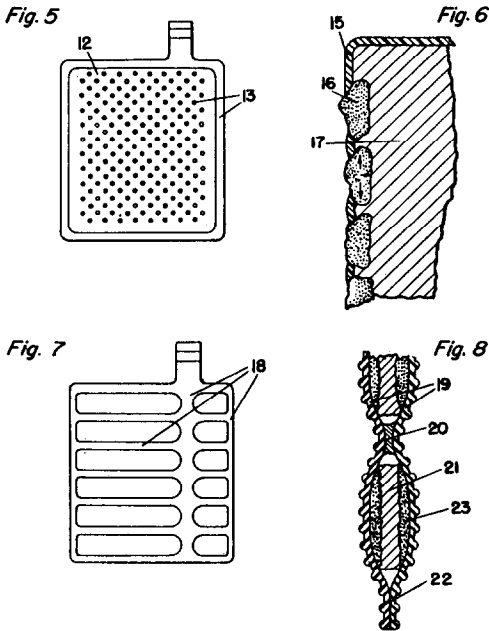


Fig. 2. Design of lead/acid battery as proposed by K. Ruetschi and P. Ruetschi [1].

say, the battery never reached a commercial stage. This is just to illustrate that not all of my research projects were successful.

After having spent one year with Professor Delahay at Louisiana State University in Baton Rouge, I joined the Electric Storage Battery Company (ESB) in Philadelphia in 1955. From then on, I was involved in a number of investigations relating to lead/acid batteries. One of my first studies in this field was the development of fuel-cell type auxiliary electrodes, for gas consumption in sealed lead/acid cells. Another area of research was the study of corrosion phenomena and the composition of multilayer corrosion films on lead and lead alloys.

In a paper, coauthored by B.D. Cahan,  $\alpha$ - $\text{PbO}_2$  was reported to exist in corrosion films. Several studies were devoted to the difference in electrochemical properties between  $\alpha$ - and  $\beta$ - $\text{PbO}_2$ . In an effort to build maintenance-free batteries, the self-discharge processes that occur in lead/acid cells were analysed in detail.

In 1964, I returned to Switzerland and joined Leclanché SA, a small manufacturer of many types of batteries. Work carried out during my time with Leclanché included a quantitative description of the pH-gradient that exists in corrosion layers. In recent years, I have developed a cation-vacancy model for  $\text{PbO}_2$ ; this relates the defects in the crystallographic structure to electrochemical properties.

My work was stimulated by many contacts with other scientists, especially at meetings such as the one held here in Varna, thanks to the Bulgarian Academy of Sciences and, in particular, thanks to Professor Pavlov and his coworkers. Contacts

provide new ideas. Without contacts, the performance suffers; there is premature capacity loss!

May I say a few words on the importance of contact between grid and active mass, and between particles in the positive plate of the lead/acid battery. A particle can only be discharged when it is in electronic contact with other particles and, through them, with the grid. If, during discharge, the contact is interrupted, because of the conversion of the contact areas from (conducting)  $\text{PbO}_2$  to (insulating)  $\text{PbSO}_4$ , the remaining  $\text{PbO}_2$  in that particle cannot be discharged. Here, it should be understood that 'particle' can also mean an 'agglomeration of particles'. It is instructive to discuss the contact between particles in terms of active material porosity. The less porous the active material, the better is the chance for good contact. In dense active material, acid access is decreased, and the capacity is acid limited. By the way, plates of high density also have high  $\alpha\text{-PbO}_2$  contents, since their interior remains at a high pH during the initial stages of formation, and since  $\alpha\text{-PbO}_2$  forms preferentially in locations of high pH, that is, in locations protected from the ingress of acid by semipermeable  $\text{PbSO}_4$  layers. In the early literature, it had been reported that  $\alpha\text{-PbO}_2$  has a lower capacity per unit weight than  $\beta\text{-PbO}_2$  [2-4]. However,  $\alpha\text{-PbO}_2$  showed a lower surface area than  $\beta\text{-PbO}_2$ . Indeed, per unit of surface area,  $\alpha\text{-PbO}_2$  gave a higher capacity than  $\beta\text{-PbO}_2$  (Fig. 3). On the basis of theoretical considerations also,  $\alpha\text{-PbO}_2$  is expected to yield a higher capacity, since it is known to have a highly defect lattice structure, from which  $\text{Pb}^{2+}$  ions can be released more readily. Comparing materials of equal surface area, that is of equal particle size, and under conditions of equal acid access, the  $\alpha$ -modification shows, in fact, a higher capacity [5].

Consider now, a high-porosity plate. Acid will penetrate it easily. Initial formation will therefore produce more  $\beta\text{-PbO}_2$ . For very porous plates, the capacity is limited only by the amount of  $\text{PbO}_2$  present. Even in most favorable case, however, the utilization factor cannot exceed about 0.65 to 0.70. At this point, the remaining  $\text{PbO}_2$  is isolated by  $\text{PbSO}_4$ .

Figure 4 depicts schematically how the local capacity, in terms of  $\text{Ah cm}^{-3}$  of active mass, depends on active-mass porosity. At low porosity, the capacity is limited by acid supply. The line  $B_0$  represents the capacity, when only the acid present initially in the pores, is thought to be available.  $B_1$ ,  $B_2$ , etc. indicate conditions where acid supply, due to diffusion and convection, provides  $\delta$  times the amount of acid present

TABLE 1. MAXIMUM CAPACITY OUTPUT AND UTILIZATION FACTOR OF  $\alpha$ - AND  $\beta$ - $\text{PbO}_2$

		$\alpha\text{-PbO}_2$	$\beta\text{-PbO}_2$	Dimension
Max. cap. output	$Q_{\max}$	0.135	0.164	A-hr/g $\text{PbO}_2$
Max. utiliz. factor	$\eta_{\max}$	0.60	0.73	( $Q_{\max}/Q_{\text{theor}}$ )
Max. cap. output per unit of internal surface	$\frac{Q_{\max}}{\text{S.A.}}$	0.035	0.022	A-hr/m <sup>2</sup>

Where  $Q_{\text{theor}} = 0.224 \text{ A-hr/g PbO}_2$   
and S.A. = specific B.E.T. surface area ( $\text{m}^2/\text{g}$ ).

Fig. 3. Extract from 'Discharge Capacities of Alpha-and Beta-Lead Dioxide Electrodes' [3].

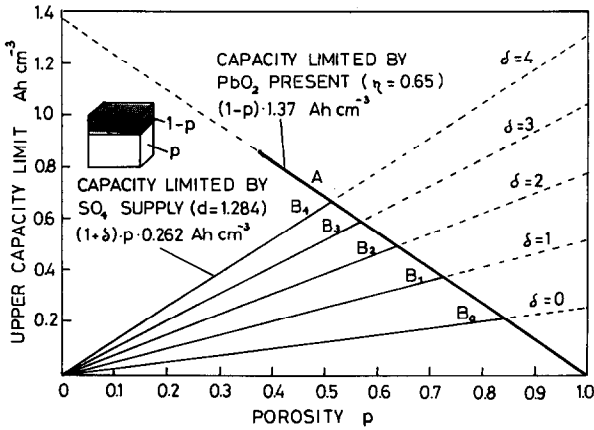


Fig. 4. Dependence of local capacity on active-mass porosity.

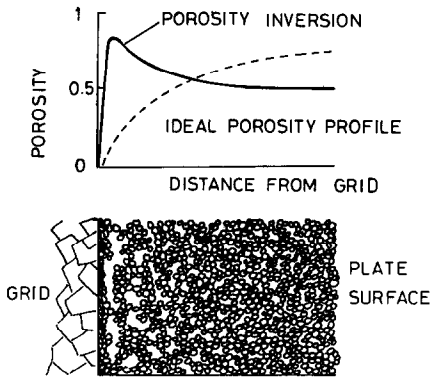


Fig. 5. Porosity inversion for positive active material.

initially in the pores. The factor  $\delta$  is determined by the discharge rate and the acid volume outside the plates, or by the flow-through rate, in case of force flow-through.

Line A represents the upper limit of capacity as given by the available  $\text{PbO}_2$  present, assuming a utilization factor of  $\nu = 0.65$ . Below a porosity of  $p = 0.37$ , the pore volume becomes so small that it is filled entirely with  $\text{PbSO}_4$  when the  $\text{PbO}_2$  is discharged to  $\nu = 0.65$ . Thus,  $0.85 \text{ Ah cm}^{-3}$  is a theoretical upper limit of the possible volumetric capacity.

The point I would like to make is the following. In modelling positive-plate performance, it has usually been assumed that there is a constant porosity throughout the plate, and that the plate surface is exposed to bulk electrolyte, that is to a pore of infinite size. Now, should cracks, splits or voids appear near the grid (e.g., as a result of inadequate pasting or drying, or as a result of grid growth) local porosity in that critical region could possibly become quite high. Notwithstanding current distribution, the grid/active-material interface region could then receive so much acid as to reach conditions of line A. Once the active material in the interface region is exhausted, discharge in the bulk of the plate will be stopped. The ideal porosity profile (Fig. 5) would thus be one with a dense 'Kugelhaufen' (and corrosion) layer near the

grid, such that acid access to the interface region is limited. Any porosity inversion, as depicted in Fig. 5, should be avoided, since it could lead to premature capacity loss. During cycling, discharge rate and charge rate, as well as temperature, could possibly influence the porosity profile, since the deposition of  $\text{PbO}_2$  occurs via a dissolution-precipitation reaction. A dense interface region could, for instance, be formed initially on the grid by electrodeposition of  $\text{PbO}_2$  from solutions with increased  $\text{Pb}^{2+}$  ion solubility and additives such as  $\text{Sb}^{3+}$ ,  $\text{Sb}^{2+}$  and  $\text{Cu}^{2+}$  that influence the electrocrystallization of  $\text{PbO}_2$ .

Let me conclude this short address by coming back to my key work 'contact'. The importance of this term is underlined in the English language by the number of synonyms in Roget's Thesaurus: 'contact' = proximity, contiguity, contiguouness, apposition, abuttal, abutement, juxtaposition, touching, meeting, conjunction, adhesion, adhesiveness, adherence, cohesion, cohesiveness, coherence, conglomeration, aggregation, closeness.

May I thus encourage you to keep good contacts with colleagues and to combine ideas. Could 'Mr. Kugelhaufen' possibly get friendly with 'Ms Corrosion Layer'?

I am grateful for the good contacts I have had with many friends present here. May I express again my thanks to all of you, and let me wish you, above all, good contact with that universal spirit of love and wisdom who has called us all into existence.

## References

- 1 K. Ruetschi and P. Ruetschi, *US Patent Applic. No. 2 883 443* (July 13, 1956).
- 2 V.H. Dodson, *J. Electrochem. Soc.*, 108 (1961) 401, 406.
- 3 E. Voss and J. Freundlich, in D.H. Collins (ed.), *Batteries*, Pergamon, Oxford, 1963, p. 73.
- 4 P. Ruetschi, S. Sklarchuk and R.T. Angstadt, in D.H. Collins (ed.), *Batteries*, Pergamon, Oxford, 1963, p. 89.
- 5 P. Ruetschi, *J. Electrochem. Soc.*, 139 (1992) 1347.