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Abstract

The Workshop was organized by the Dresden University of Technology. The leaders of the organizing committee were K. Wiesener and J. Garche. The meeting brought together 48 scientific and industrial experts from 16 countries to define and assess the major problems that presently limit further development of the lead/acid system. In particular, support from the UNESCO Regional Office of Science and Technology for Europe and North America (ROSTENA) and from VARTA, GRACE, DETA, BOSCH, DIGATRON and Zwickauer Batterie GmbH allowed delegates from both the east and west to join together in open debate in the pleasant environment of Gaussig Castle near Dresden. The scientific programme was divided into three main topics of special interest: modes of battery failure, reactions at the grid/active-material interface, problems with valve-regulated 'sealed' lead/acid batteries, and into two further topics of general interest: modern measurement methods, modern technology and new materials.

Modes of battery failure

The introductory address* was given by D. A. J. Rand (CSIRO, Australia), the co-author of the paper was B. Culpin (Chloride Industrial Batteries, U.K.). Specific failure modes were discussed in terms of the influence of the required charge/discharge duty (i.e., float, cycling or automotive), the design of cell (i.e., flat- or tubular-plate, flooded- or immobilized-electrolyte), and the choice

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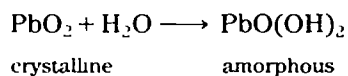
of grid alloy (i.e., lead-antimony or lead-calcium). It was pointed out that the failure modes of valve-regulated batteries (VRBs) are likely to differ from those of flooded-electrolyte systems. For example, grid corrosion and growth are generally considered to be of major importance in VRBs. Both negative-plate sulfation and water loss are also of concern, particularly in cycling applications. By contrast, traditional problems associated with shedding, mossing and dendritic growth of the active material should be reduced in VRBs. Dr Rand emphasized the need to distinguish between *catastrophic failure*, as characterized by a sudden inability of the battery to function, and *progressive failure*, as demonstrated by some more subtle deviation from optimum performance. Catastrophic failure usually arises from incorrect cell design, poor manufacturing practice, abuse, or misuse. Progressive failure is more difficult to predict and explain, it is generally caused by microscale changes in plate characteristics brought about by the influence of component selection, manufacturing variables and service conditions.

F. Bottcher and H. S. Panesar* (VARTA Batterie AG, F.R.G.) presented an interesting model to explain the capacity loss of the positive electrode during charge/discharge cycling. The electrode was divided into a set of sub-systems that, simultaneously, determine the performance features of the system, namely:

- electrolyte/PbO₂ interface
- PbO₂ crystal properties
- macro- and micro-structure of the active material
- PbO₂/grid interface

Each sub-system is characterized by different physical parameters that vary during cycling and are inter-related. Analytical methods employing univariate and exploratory multi-parameter statistics have proved to be efficient tools for determining the most significant of the parameters. These critical parameters can be used to define the state of the positive mass.

The failure mechanism of the positive electrode was examined by D. Pavlov (Central Laboratory of Electrochemical Power Sources, Bulgaria) in terms of the micro-scale properties of the PbO₂ active material. Using a transmission electron microscope (TEM), crystalline zones of both α -PbO₂ and β -PbO₂, together with amorphous zones, were found in particles of charged PbO₂. The average dimensions of the crystal zones were between 400 and 600 Å. The proportion of amorphous material can be increased by hydration, i.e.,



The transformation between crystalline and amorphous materials is reversible. Thus, the PbO₂ is an open system, i.e., there is a transfer of ions between the solution surrounding the particles and the hydrated zones. The kinetics of the amorphization process (as measured by X-ray diffraction analysis of

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the changes induced in the crystalline zones) is influenced by different cations (e.g., antimony). It was also discovered that the amorphous zones grow with increasing oxygen content of the PbO_2 particles and that this causes an increase in the polarization of the electrode.

W. Bohnstedt (GRACE GmbH, FRG) analyzed the effect of antimony poisoning in lead/acid batteries. The phenomenon was investigated using rotating disc electrodes and reported as a function of negative electrode potential and time. Examination of different expanders showed that it is possible to suppress hydrogen evolution. Special inhibitors, based on aromatic compounds, were tested and a model was proposed for the mechanism by which the specific adsorption of these compounds at the negative electrode suppresses the generation of hydrogen. Such inhibition is beneficial in that the potential of the negative electrode does not decrease and purging of antimony is possible over a large number of charge/discharge cycles.

The session concluded with communications from P. Brandt and K. Baumgarten (Volkswagen AG, FRG) that provided

- an overview of battery problems encountered in field service
- a comparison of the performance of automotive batteries, employing sheet or envelope separators, in a practical field test
- photographs of failures typically exhibited by automotive batteries

The most important conclusions drawn from the above presentations and the accompanying discussion were

- batteries exhibit a very wide diversity of failure modes
 - envelope separators are superior to their sheet counterparts
- Some of the failure modes were debated in great detail, particularly those associated with premature capacity loss. The deliberations highlighted the marked sensitivity of battery performance to changes in cell technology and design, as well as to plate-processing and battery-operating procedures. The information gathered provides a valuable resource to both battery scientists and manufacturers.

Reactions at the grid/active-material interface

J. Garche (formerly Dresden University of Technology, now ZSW Ulm) presented an introductory overview of phenomena occurring at the interfacial region between the grid and the active material in the positive electrodes of lead/acid batteries. This complex system was discussed in terms of a reaction between the lead grid and the PbO_2 active material. The reaction kinetics are determined primarily by the features of this interfacial region, especially by the

- composition profile in the interfacial region
- thickness and porosity of the interfacial region
- operating conditions of the electrode
- grid material

- electrolyte
- temperature

The influence of each of these parameters on the electrochemical behaviour of the positive electrode was analyzed. It was argued that the positive electrode at open-circuit is a *dynamic system* in which a passivation reaction (i.e., a solid-state equilibration reaction) and a depassivation reaction (i.e., a liquid-phase H_2SO_4 concentration cell reaction) take place. The rate of the depassivation reaction is determined by the H_2SO_4 concentration. In concentrated H_2SO_4 , the depassivation rate is high and, consequently, passivation of the electrode is not observed. In dilute H_2SO_4 , the depassivation rate is low and passivation will occur.

The characteristics of the boundary between the grid and the active material were examined by A. Winsel (VARTA Batterie AG, F.R.G.). Attention was drawn to the

- purpose of the grid
- preparation and formation of the boundary layer
- phenomenon of thermo-passivation
- boundary layer as active material
- boundary layer and the antimony-free effect
- binding of 'PbO₂-Kugelhaufen' to the grid

Of particular interest was Professor Winsel's view of the antimony-free effect (see discussion below).

C. V. D'Alkaine (Grupo de Electroquímica e Polimeros, DQ-UFSCar, Brazil) described studies of passivating films on lead in sulfuric acid. A voltammetric method was used to investigate the characteristics of different types of films that were formed under various conditions on both lead and Pb-Ca and Pb-Sb alloys. A general model was proposed to interpret the phase transformations taking place in the anodic and cathodic regions.

Z. Takehara (Kyoto University, Japan) described the reduction and oxidation of lead sulfate crystals in sulfuric acid solution. It was concluded that the reduction reaction is controlled by mass transfer of Pb^{2+} ions supplied by the PbSO_4 crystals. By contrast, the oxidation reaction is limited by a charge-transfer process.

G. Sundholm (Helsinki University of Technology, Finland) discussed the influence of antimony on the anodic oxidation of lead in sulfuric acid. In addition to conventional electrochemical methods, Dr. Sundholm has used ring-disc electrode, X-ray diffraction and photoelectrochemical spectroscopic techniques. These revealed the participation of soluble Pb(IV) species as an intermediate in the oxidation of PbSO_4 to PbO_2 , as well as during the reduction of this oxide.

D. Pavlov and B. Monanov (Central Laboratory of Electrochemical Power Sources, Bulgaria) reported the existence of three antimony lead oxides that have a high photoactivity and a high conductivity. $\text{Pb}_{(1-x)}\text{Sb}_x\text{O}_2$ is reduced at a potential that is more negative than the reversible value for the $\text{PbO}_2/\text{PbSO}_4$ transformation. Therefore, this substituted oxide can provide the corrosion layer with higher conductivity in a more negative potential range.

This allows current to flow via the corrosion layer during deep discharges of the active mass. Hence, Pb-Sb grids improve the capacity of the positive plate.

R F Nelson (Portable Energy Products, U S A), K Takahashi* (Matsushita Battery Ind Co , Japan), and H Doring and J Garche (Dresden University of Technology, F R G) examined the influence of tin on the passivation of the grid/active-material interface. It was shown that tin can be employed to avoid passivation. This action is influenced, however, by the tin level, the method of tin addition (i.e., alloying, electrochemical, chemical or mechanical plating), the weight ratio of H_2SO_4 to PbO_2 , and the antimony content of the alloy.

Discussion amongst the delegates centred largely on the antimony-free effect (AFE). This is typified by a premature capacity decay of 25 to 30% of the initial value that occasionally occurs during charge/discharge cycling of lead/acid batteries. The phenomenon is unequivocally associated with processes taking place at the positive electrode. It cannot be attributed, however, to any visible deterioration of the positive active material structure or to insufficient charging. In particular, the AFE is observed as an early degradation in capacity during cycling when (i) charging is performed at low current densities, i.e., at the $C/20$ rate, (ii) overcharge is applied for an extended period, i.e., at charge factors of 1.2 or more.

The AFE disappears and the original capacity is restored under the following conditions:

- when a special charging regime is applied during cycling, i.e., 70% recharge at high rates ($C/2$ to $C/3$), 30% at low rates ($C/20$), overcharge less than 1.2
- an open-circuit stand for about 2 to 3 months
- after a low-rate discharge without potential reversal
- spontaneously after addition of $SnSO_4$ solution to the electrolyte in the charged state (in the case of Planté electrodes only)
- after washing and drying a fully-charged plate and then applying an immediate discharge when returned to the electrolyte

The capacity decay can be annulled when the charge regime during cycling is changed from a low rate to a high-rate/low-rate charge within about 20 cycles under ELOFLUX conditions (i.e., flow-through conditions). The AFE has been observed on positive plates of various design, such as Planté, tubular and pasted plates.

The AFE can also occur (and be removed) in the presence of antimony, e.g., when Pb-Sb alloys are used as grid materials. For this reason, it has been suggested that the term 'antimony-free effect' is not appropriate. In a recent publication, it was advanced that the phenomenon is better described as a relaxable insufficient materials' utilization (RIMU). Nevertheless, this and other proposals were not generally accepted by the meeting. Notwithstanding, the term RIMU is used in the remainder of this report.

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A controversial point in the discussion was the exact location of the effect. Many authors claim that the origin lies in the corrosion layer. In the absence of antimony, the resistance of the corrosion layer is increased markedly during deep discharge as a result of the reduction of the PbO_2 corrosion layer to PbSO_4 . Therefore, the electronic path through the corrosion layer to the active mass becomes blocked. It appears that antimony can hinder the complete transformation of the corrosion-layer PbO_2 to PbSO_4 through the formation of PbSO_4 that has a fine-crystal structure (J. Garche). Another explanation of the influence of antimony is the formation of $\text{Pb}_{(1-x)}\text{Sb}_x\text{O}_2$ — a compound that is reduced at a more negative potential than PbO_2 (D. Pavlov and B. Monachov). Others (R. J. Hill and D. A. J. Rand) suggest that antimony exerts a beneficial effect on the mechanical integrity of the corrosion layer, i.e., it modifies the degree and nature of crack formation. Nevertheless, the VARTA group has found that RIMU can easily occur in the presence of antimony, and that it correlates more closely with the conductivity of the active material than with the conductivity of the grid/active-material interface. Therefore, the VARTA group has proposed that RIMU does not result from either the formation of a non-conductive layer at the grid/active-material interface, or from the development of cracks in the corrosion layers surrounding the grid wires. It is argued that the various phenomena described above can be explained qualitatively by the so-called *Kugelhaufen Model* developed by Professor Winsel. In this model, it is assumed that the non-conductive layers around the grid wires are the result of a non-uniform current distribution across the active material, in other words, the non-conductive layer is a *consequence* of RIMU rather than its origin.

In conclusion, it is clear that knowledge on RIMU has been advanced considerably. At present, RIMU can be readily avoided, generated, or removed by known methods that are only effective when the positive active material is in a firm state and is fully charged after each cycle. Clearly, this knowledge is of high practical relevance to all types of lead/active batteries operating on a cycling regime, and in particular to VRBs.

Problems with valve-regulated 'sealed' lead/acid batteries

This session opened with a paper on VRBs by K. Wiesener (Dresden University of Technology, F.R.G.). For these batteries, it was pointed out that whereas oxygen is easily consumed during overcharge, the build-up in hydrogen pressure poses more of a problem. Hydrogen cannot recombine at the positive electrode because it is blocked by sulfate adsorption and, therefore, other methods for its removal must be devised. Possibilities include the use of auxiliary electrodes or gas-phase catalysts, but these suffer from problems of complexity, cost and inactivation. Alternatively, hydrogen evolution can be suppressed by lowering the charging voltage through the incorporation of excess negative active material, increases in hydrogen

overtoltage via the use of pure materials, or the employment of hydrogen-evolution inhibitors. Professor Wiesener also stated that hydrogen generation can be minimized by optimization of the oxygen recombination process so that the negative electrode is maintained at a low potential. In gelled-electrolyte cells, this is achieved by promoting the formation of cracks in the gel. In glass-mat designs, the technology is directed towards lowering the degree of filling to a point where gas transport is maximized without loss of discharge capacity. The following are necessary for the development of a truly 'sealed' lead/acid cell

- optimization of the oxygen-recombination efficiency
- minimization of the hydrogen overcharge current
- promotion of hydrogen oxidation by direct oxidation, or by the use of gas-phase catalysts

J Mrha (J Heyrovsky Institute, Czechoslovakia) compared the oxygen recombination properties of nickel/cadmium and lead/acid systems and demonstrated that the former exhibit a higher efficiency. For lead/acid, it was claimed that there is a need for either a catalyst external to the plate stack, or for the creation of a thin-film condition within the plates. Further, compression of the plate stack may be critical if good oxygen-recombination is to be achieved in such cells. Dr Mrha proposed a typical value of ~ 10 kPa (1.5 psi). Under normal conditions, electrolyte first fills the plate pores and then enters the separator. Electrolyte dosing and compression must, however, be kept within practical limits to optimize oxygen recombination and thus lower the gas pressure within the cell. At extremely high compression levels (65 kPa), gassing oscillation at the negative plate can be observed.

R F Nelson (Portable Energy Products, U S A) focused his presentation on the 'almost starved/almost flooded' condition in VRBs and analyzed how this influences gassing and polarization, particularly at the negative plate. Scientific evidence was provided for the frequent observation of a bimodal voltage distribution in multi-cell strings, where some cells are depolarized due to oxygen recombination while others are polarized into the hydrogen gassing region. Thus, at float voltages below the hydrogen gassing level (2.37 to 2.35 V), some cells will be venting hydrogen. Cell-to-cell voltage variations of 150 to 200 mV are encountered and this can be traced to the electrolyte distribution within a given cell and to differences in the state of the negative electrodes. Some negatives will behave as if 'flooded' and, therefore, will polarize easily and evolve relatively large amounts of hydrogen. Others will be 'dry' and, consequently, will be difficult to polarize. While the latter may recombine oxygen very efficiently, such cells may be more susceptible to thermal runaway. Dr Nelson proposed that the best design for VRBs may be one where a 'mixed potential' exists at the negative plate and there are concurrent moderate levels of oxygen recombination and hydrogen gassing.

H Dietz (Dresden University of Technology, F R G) concentrated on the problem of hydrogen gas generation during overcharge of VRBs, and the lack of dissipation of the gas via oxidation or diffusion through the cell walls. It was pointed out that direct oxidation is hindered by sulfate and

oxide adsorption, but that the overpotential is lowered by the presence of α -PbO₂. The author measured appreciable hydrogen oxidation on the positive plate at potentials of 1.57 V versus Hg/Hg₂SO₄ and proposed that higher oxidation currents are observed at increased hydrogen gas concentrations. Under normal conditions, it was concluded that hydrogen recombination cannot be realized by practical means. Excellent hydrogen consumption capabilities were shown for two catalysts, namely, platinum/activated carbon and tungsten carbide/activated carbon. The platinum catalyst performed extremely well but was costly. The tungsten carbide catalyst was found to operate satisfactorily in lead/acid cells, especially when hydrogen was in excess relative to oxygen.

In summary, gas management appears to be the main problem area for VRBs. A wealth of interesting data were given to show how oxygen recombination facilities can be put to good use in these products. The picture is not so bright for hydrogen gas management. Given that hydrogen generation will almost always occur, several proposals were put forward to reduce its build-up in VRBs.

Modern measurement methods

K. R. Bullock (Johnson Controls, U.S.A.) presented new methods for the examination of the corrosion layer. These techniques include laser Raman spectroscopy, photocurrent and photoacoustic spectroscopy, and solid-state electrochemical procedures. The laser Raman spectroscopy can readily identify tetragonal and orthorhombic PbO (i.e., α -PbO and β -PbO), basic lead sulfates and PbSO₄. Microprobe laser Raman spectroscopy is a particularly valuable technique and can be used to resolve the composition of corrosion layers down to 2 μ m in thickness. Equally useful are the methods of photocurrent (pc) and photoacoustic (pa) spectroscopy as these allow the detection of PbO (pc, pa) and basic lead sulfates (pa) in the corrosion layer. For example, it has been found that β -PbO forms before the development of the α -PbO layer.

S. A. Campbell and L. M. Peter (Southampton University, U.K.) described the application of photocurrent spectroscopy in studies of the anodic polarization of lead in acid and alkaline electrolytes. The results confirm that a film of α -PbO is formed underneath the passivating sulfate film. Using the technique, it is possible to follow the cycling of PbO to PbO₂ and back again, *in situ*, by monitoring the photocurrent response as a function of potential.

The value of the impedance technique in the investigation of electrochemical porous systems, especially the negative electrode of the lead/acid battery, was illustrated by K. V. Rybalka (A. N. Frumkin Institute of Electrochemistry, U.S.S.R.). A comparison was made of the pore volume of the negative active mass obtained by the impedance method (the electrochemical active porosity) and by the standard porosimetry procedure.

M Calábek (Brno University of Technology, Czechoslovakia) reported on an *in situ* method to measure the resistance of the grid/active-material interface

N Niepraschk (Dresden University of Technology, F R G) described an ingenious ultrasonic method for the investigation of the corrosion layer on lead and lead alloys This method provides information on the internal mechanical stresses in the layer and, therefore, on the porosity

R Kiessling (DIGATRON, F R G) focused his presentation on techniques for battery testing It was argued that a computer-controlled system provides the best method for evaluating different battery types In this respect, the capabilities of the DIGATRON BTS 500 testing equipment were described in detail

Modern technology and new materials

In the introductory overview, J Kwasnik (Central Laboratory of Batteries and Cells, Poland) and P Rakin* (Chemical Power Sources Institute, Yugoslavia) outlined the newest developments in battery technology Attention was directed to grid alloys, grid design, continuous grid-casting methods, expanded and copper grids, separators, granular oxide for tubular plates, forced electrolyte flow, and bipolar designs The conclusions were as follows

- extensive work is in progress on cell design and technology
- advanced materials are under evaluation
- automation improves safety in production
- ecologically clean processes for material recycling increase competitiveness

W Bohnstedt (GRACE, F R G) gave a comparative summary of the essential characteristics of the different separation systems for automotive and industrial batteries It was noted that, at present, more than 50% of modern batteries use pocket separators made from microporous polyethylene

The production of new material for current-conducting components in lead/acid batteries was discussed by A I Rusin** (Metallurgy and Beneficiation Institute, U S S R) Copper and aluminium grids, well protected by a covering of lead, provide gains in battery performance

K R Bullock (Johnson Controls, U S A) presented a method to enhance the formation of positive plates In this process, the surface of unformed plates is treated with ozone in order to convert lead oxide to conductive lead dioxide Good oxidation of the free lead in the paste is also achieved

Finally, J Yamashita† (Yuasa Battery Co , Japan) provided a detailed account of the development of sealed lead/acid batteries in the Yuasa Battery Co

As noted throughout this report, several of the papers presented at the Workshop will be published in this Journal

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