BATTERY TESTING IN GERMANY

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1. Introduction

A number of contributions on testing of various batteries will be presented in the course of the next 3 days by several of the competent and experienced German colleagues attending this meeting, who will provide, in total, an overview of recent developments in testing and on results obtained in Germany.

For this reason, and so to speak as an *avant-propos*, it might be worth presenting some general considerations on, and some special aspects of, testing, which hopefully will be of use for professional testers and designers of new standard specifications. In order to simplify matters, the following comments are restricted to lead–acid cells and preferably to cyclic endurance tests on these cells.

The reasons for this restriction are evident:

— The lead–acid cell is the oldest rechargeable system It embodies a tremendous amount of experience and R + D results. It may serve also as an example for other systems.

— The theory of the cyclic endurance test is understood less than any other specified test. The results obtained by endurance tests in general depend on many parameters, a number of which is collected in Fig. 1. It clearly demonstrates the complexity of the problem and is self-explanatory as to why marginal attempts only have so far been made to develop a basic mathematical theory.

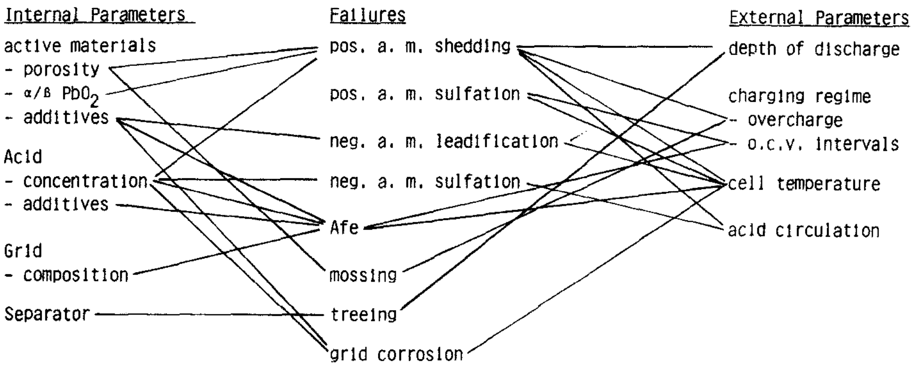

Fig. 1. Relationship between internal and external parameters and failures occurring in cycle life testing.

In DIN and IEC specifications for traction batteries, for instance, and this is true also for other standard specifications, the mechanism of failure is never queried. This might be acceptable for standard specifications, but for R + D it is of vital interest to obtain as much information on failures as possible. Therefore additional measurements and post-test investigations are necessary.

Experience has shown that most of the failure modes observed in lead–acid cell life testing depend on several parameters simultaneously. This is schematically shown in Fig. 2 which appears to be even more complex than Fig. 1.

In a few of these cases (Fig. 2) systematic investigations of the effect of some of these parameters on life and failures have been published in the literature. Some of them will be discussed in some detail.

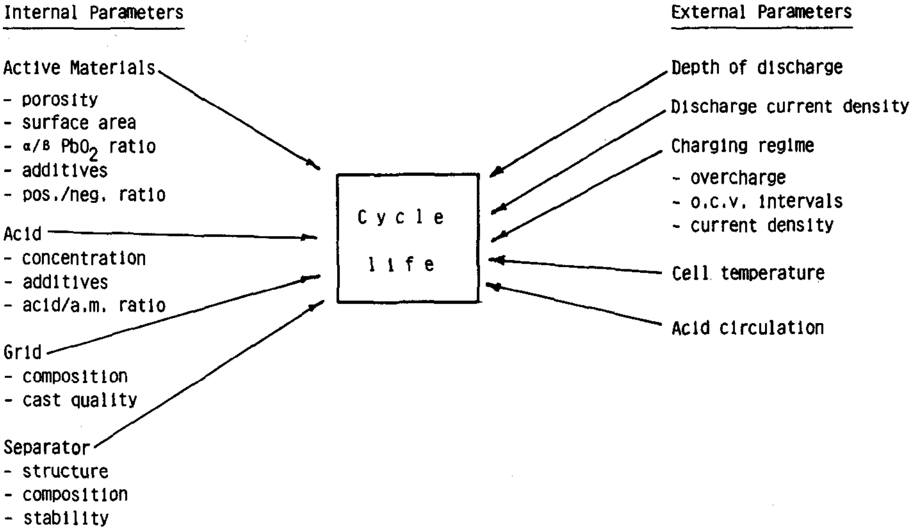

Fig. 2. Parameters affecting the endurance of lead–acid cells.

2. Effect of temperature on cycle life

In the early papers of Macholl and Koch [1] (1956) and of Lander [2] (1958), both dealing with SLI batteries, it was shown that the cell temperature has a remarkable influence on the number of cycles obtained in an SAE test, which at that time was:

Discharge	20 A 1 h
Recharge	5 A 5 h
Temp.	43 ± 2.8 °C
20 h capacity test	each week
Failure	capacity lower than 40% of rated 20 h capacity

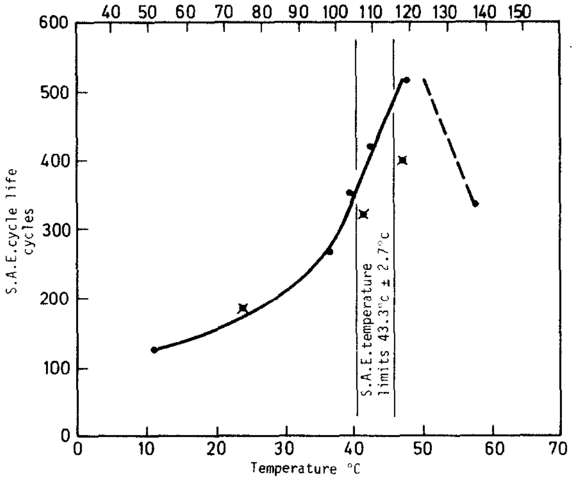

Fig. 3. Relationship between S.A.E. cycle-life and temperature (S.A.E. group 4N, parallel plate cell, 50 A h capacity). ✖ Data of Lander (1958).

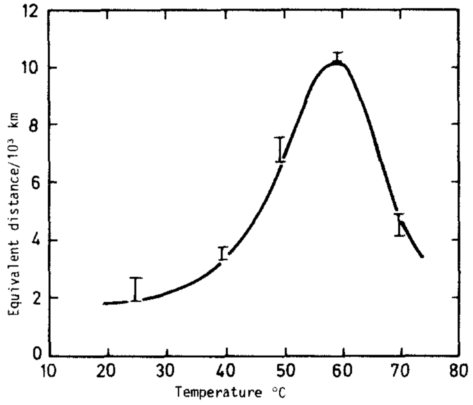

Fig. 4. Service life (equivalent km) of lead/acid batteries under simulated electric-vehicle service using BATTRONIC/AEVA profile as a function of temperature of operation [3].

The results of Macholl and Koch are given in Fig. 3. They agree rather well with Lander's data of 1958. As can be seen, the cycle numbers show a distinct optimum around 50 °C. Macholl and Koch found in a post-test examination that at temperatures above 50 °C the negative electrode begins to limit the life. Higher temperatures reduce the shedding of positive active material and increase the tendency to form hard, granular (sulphated) lead in the negative electrode. At temperatures lower than 50 °C the positive electrode limits the life due to shedding.

A few months ago our Australian colleagues [3] published results obtained on traction batteries which had been cycled at various temperatures on a driving cycle. Their results are presented in Fig. 4. Again, it is shown that there is an optimum life, this time at a temperature of about 60 °C. The failures observed at the 70 °C test were identified as being due to negative plate swelling and mossing, and positive grid corrosion, apparently different from the observations of Macholl and Koch.

These results suggest that:

The cycle life of cells is very sensitive to temperature variation. On the other hand, the IEC standard specifications allow a temperature range of 5 °C for SLI and 33 - 43 °C for traction batteries. Are these still acceptable? Macholl and Koch have already pointed out that misleading conclusions may be drawn from cycle life results if the temperature is not closely controlled.

In any case, no attempt has been made to develop mathematical relationships between life and temperature on the basis of a theoretical model.

3. Effect of acid concentration on cycle life

Lander [2], in his paper of 1958, presented results on SLI batteries' cycle life in dependence of acid concentration. His data are given in Table 1 (Bode [4], p. 332). They show that there is a remarkable effect on life insofar as higher acid concentration decreases the cycle number.

TABLE 1

Operational life of SLI batteries*

Temperature	Operational life in cycles		
	Density: 1.240 (kg l^{-1})	1.275	1.310
24.5 ± 3	185	165	105
42 ± 1.5	300	255	130
47 ± 1	415	345	330
Life increase 1 °C	23	18	20

*Lander (1958).

Again, no attempt was made to develop mathematical relationships. The levels of acid concentrations investigated by Lander are given in terms of density in the fully charged state at the beginning of the test. It is common knowledge, however, that these concentrations do not remain constant in a practical cell, they change during discharge and charge. Since it is essential during basic investigations to keep the concentrations as constant as possible over the total test time by using a surplus of electrolyte, special test cells are needed rather than practical cells. So far, no attempt in this direction can be found in the literature. So the precise effect of acid concentration on life must be reexamined.

4. Effect of depth of discharge (DOD) on the cycle life of positive pasted plates

Huster and Voss [5] investigated the effect of DOD on the cycle life of positive pasted plates in 1967. In order to avoid the influence of any parameter other than DOD as far as possible, special test cells were used having a surplus of negative active material and of electrolyte. Positive plate potentials were controlled by an Hg/Hg_2SO_4 reference electrode. Temperature, currents, etc., were kept constant. However, the term "DOD" itself needs more detailed consideration:

— If DOD is related to the dimension A h discharged in each cycle per A h nominal capacity, it is not altogether acceptable, because the nominal capacity is defined in a rather arbitrary manner.

— If DOD is related to the dimension A h discharged in each cycle per 100% A h capacity discharged at the same rate, we are faced with the experimental problem of adjusting the DOD during the test to the actual dischargeable capacity, which obviously changes during the course of the test.

— The same is true if DOD is related to the original amount of active material — this does not remain constant during the test because of shedding.

In other words, it is almost impossible, using reasonable amounts of time and many, to carry out life experiments with a constant DOD value over the total length of the life test, except at 100% DOD.

In spite of these uncertainties, it has been found that there is a log-linear relationship between cycle number and DOD, as shown in Fig. 5. In this instance we were able to develop a mathematical model using a shedding mechanism. Perhaps this model has been oversimplified or overtreated. But

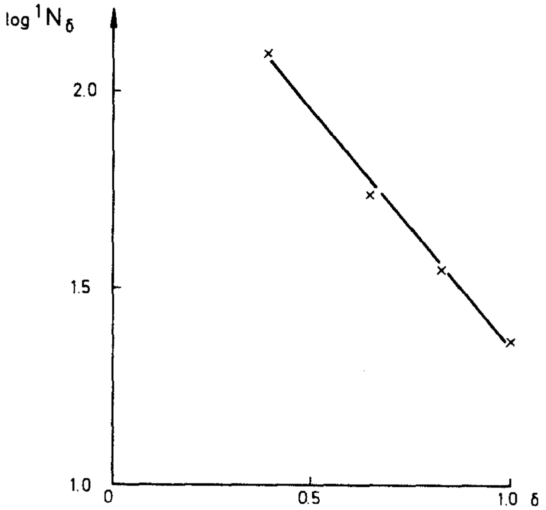

Fig. 5. Log-linear relationship between first cycle life and depth of discharge.

at that time it was a first attempt to make rechargeable battery cycle life accessible to mathematical calculations; the whole case needs a re-evaluation, however.

5. Effect of acid agitation on cycle life

Acid agitation, circulation or "flow through" of acid through the porous, active material may not be considered as a principal parameter as is, for instance, cell temperature. Any method of acid agitation serves, to a greater or lesser degree, as a means of homogenizing a number of principal internal and external parameters, such as acid concentration, cell temperature, and current density, over the whole cell. In other words, acid agitation results in a more uniform and controlled parameter distribution. Consequently, acid agitation improves and equalizes the cell behaviour and, in particular, its life.

In a recent paper Courbière and Klein [6] have shown the effectiveness of acid circulation on the acid concentration distribution of an electric vehicle cell. Their results are presented in Fig. 6. As can be seen the acid concentration in the upper portion of the cell differs from that in the lower

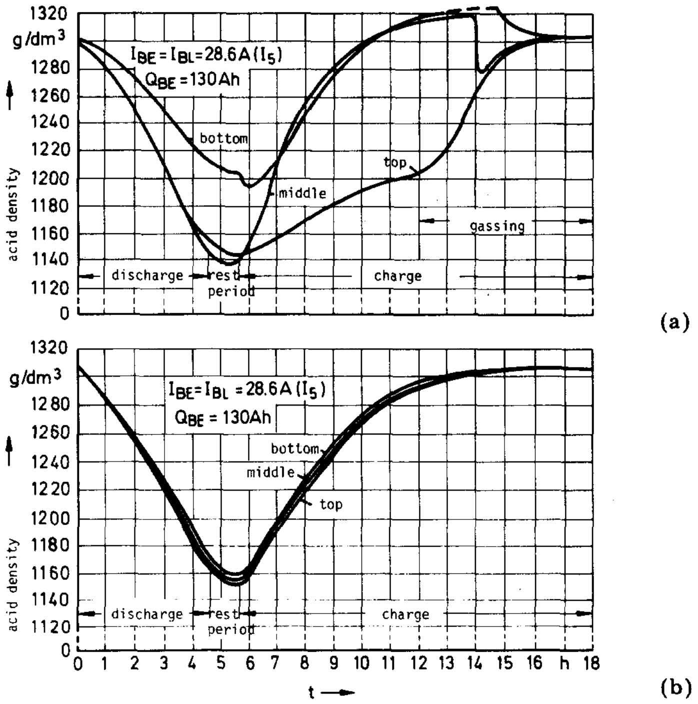

Fig. 6. Acid density at three different sites of the cell (bottom, middle, top) during cycling (a) without and (b) with electrolyte circulation.

portion of the cell when no electrolyte circulation is applied. Under certain operative modes this state of acid stratification may be maintained over many cycles, thus, obviously, affecting the cell behaviour in a negative manner. Acid concentration becomes uniform when circulation is applied.

Today there is no doubt of the beneficial effect of acid circulation on the cycle life of lead–acid cells. This has been repeatedly demonstrated, not only in bench tests, as will be shown by Prof. Winsel later in this meeting, but also practically as, for instance, in batteries for buses operated by GES.

A still more effective method than circulation is that of the forced flow of electrolyte through the pores of the active materials. This method allows tests and experiments to be carried out with a precision unachievable by any other method. For this reason we mainly use it for fundamental investigations. We hope to apply it to practical cells in the future, however.

6. Conclusions

In conclusion it may be stated that:

the cycle life of lead–acid batteries depends on many parameters; few have been systematically investigated;

mathematical modelling is complex and in an infant state;

cycle life test results, even those involving standardized tests, may lead to misleading conclusions if parameters are not kept constant within narrow limits;

temperature variations may lead to different failure mechanisms; this is important for accelerated testing;

in view of the empirical nature of cycle life testing the design of new, standardized test methods requires experience and extremely careful preparation;

the significance of bench testing for practical battery behaviour is a separate topic. It must be considered on a case to case basis.

References

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4 H. Bode, *Lead–Acid Batteries,* Wiley, New York, 1977.

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6 R. V. Courbière and F. Klein, *Electrotech. Z. Bd., 106* (1985) 542.