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Voltammetric investigations of negative lead battery electrodes: the effect of organic expanders

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By means of a continuous voltammetric sweep technique, the formation process of lead sheets in sulphuric acid can be investigated. Its behaviour depends strictly on the presence of certain organic substances. As an example, the effect of some expanders and other additives is demonstrated.

Introduction

In recent years the application of the voltammetric sweep method for the investigation of electrode processes has become quite popular. The importance of this method is emphasized by the fact that other methods are seldom suited for such studies. Many of the voltammetric investigations are concerned with the electrochemical transformation of chemisorbed molecules or with reactions in the double layer. More recently the voltammetric sweep method has been applied for investigations of reversible electrode reactions in mass electrodes, i.e. to systems which are closely related to commercial secondary-cells. For many investigations concerning reaction-mechanisms or kinetics, the assumption has been made that the processes are reversible.

We have now modified the voltammetric sweep method such that rapid cycling of an electrode can be simulated, thus permitting the observation of the mostly slow and irreversible processes at the electrode. In almost all known storage battery systems such processes do occur and lead sooner or later to the breakdown of the battery. Many attempts have been made to postpone the ageing processes of electrodes either by mechanical means or through additives to the active masses. A well-known example is the use of expander compounds which are added to the negative electrodes of storage batteries [1]. However, such additives are also in use in other types of storage batteries. The types and amounts of additives, in particular how they are added, belong to the best kept secrets of the manufacturer. If these additives are high-polymer organic compounds it is often very difficult to identify them analytically. Furthermore it is almost impossible to determine those properties which are effective in the battery. This limits the testing procedures to the final product only. Occasionally the storage battery industry uses, for technical reasons, additives which interfere with the electrode reactions. We have studied the effect of additives using the modified voltammetric sweep method [2]. Our interests are twofold: Firstly we would like to determine how uniform commercial expanders are and how effective or successful are cleaning operations (for example, the extraction of impurities). Secondly we are interested in the selection of expanders which do not interfere with the electrode reactions.

In order to avoid complications due to pore-geometry and mass-transport through pore systems we use macroscopically plane bulk electrodes of high purity lead as two-dimensional substitutes for porous electrodes. Artifacts of additives which reach the negative electrode either purposely or accidentally can be recognized relatively rapidly.

Experimental details

High purity lead electrodes in the form of sheets or rods were used. In each case the positive electrode was over-dimensioned. As reference electrode the system $Hg/HgSO_4$ was used. The sweep time for one cycle was 1 min. Sulphuric acid of the density 1·28 g/cm_3 was used as electrolyte. The current was recorded (Fig. 1 and 2). An additive (in form of a solution or suspension) was added to the electrolyte of the system which had been cycled until the amplitude of the peaks had reached a constant value. Thus we disturbed the reaction mechanism of the negative electrode and therefore modified the recorded peaks. The most intense discharge peaks ($Pb/PbSO_4$) were used for the evaluation of the curves and the constant starting value (before the addition of the testing substance) was set to 100. Ten cycles after the addition of the additive the peak intensity difference was determined.

Results and discussion

The results obtained from different huminate qualities are shown in Fig. 3. Differences can clearly be distinguished. These differences are in line with the cold start ability of batteries which have been produced with the same type of expander. Recent investigations on industrial cells have also shown a correlation with the life expectancy.

Next we will discuss the effect of various induline samples. The water-soluble portions of these products (up to 5%) interfere strongly with the charge and discharge characteristics. Products which have been well purified show a strong positive effect (Fig. 4) and no reduction in the peak height after the initial increase. Strong negative effects have also been observed with certain foaming agents. Such foaming agents are often added to the forming acid to reduce the acid spray (Fig. 4).

With the above-described method it is possible to determine whether additives which are deposited on the negative plates influence the reaction mechanisms in a positive or negative way. It is also possible to test other compounds and their effectiveness using this method. For example, phenols are known to have a positive effect [3, 4]. However, we find that the positions of the OH-groups with respect to each other as well as with respect to other substituents influence the activity measurably.

The expanders used in the production so far are derived from natural products. They are therefore only poorly characterized and do not always show the desired effect and uniformity. Therefore, it would be of advantage to use synthetic expanders which could be investigated

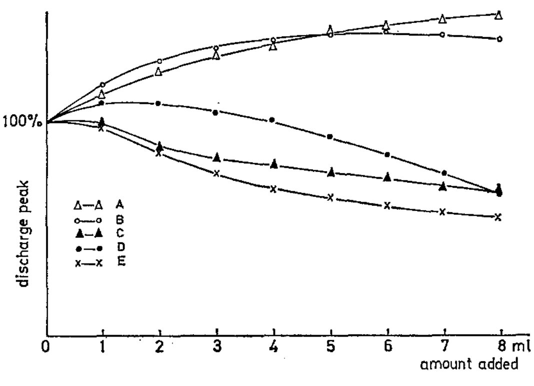

Fig. 3. The effect of sodium huminates of different quality on the peak height. Added solution 1 g in 100 cm³ sulphuric acid or water.

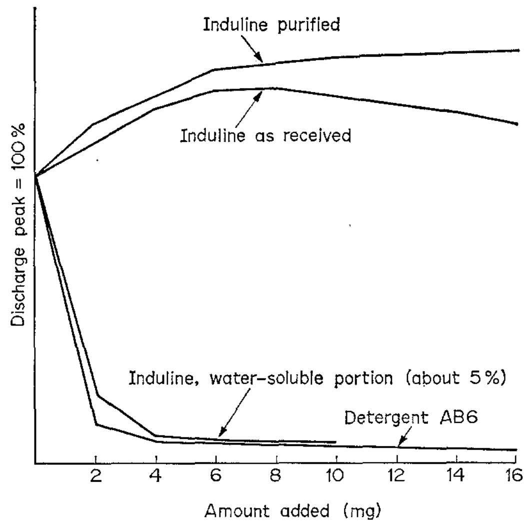

Fig. 4. The effect of different additives on the discharge peak height.

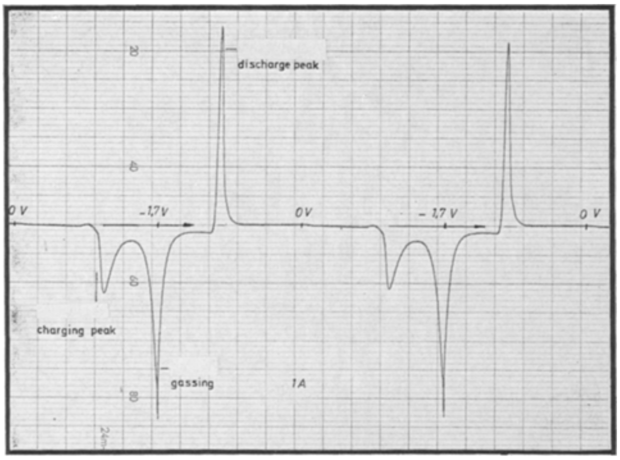

Fig. 1. Voltammetric charge and discharge of lead metal sheets. Potential against the $Hg/HgSO_4$ electrode. Each cycle lasts 1 min.

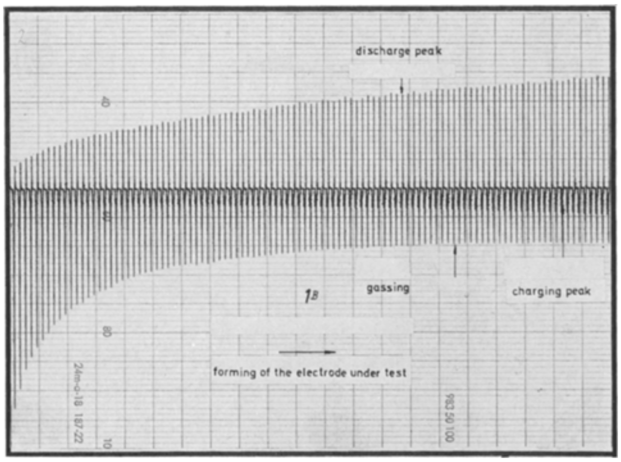

Fig. 2. Sequential voltammetric sweeps, as in Fig. 1 but with slower chart speed, demonstrating the progressive formation.

on the basis of their structure. One may still expect difficulties due to the fact that the processes which occur at the negative electrode are not too well known. It may also be mentioned that the range of applications for this method is very large due to the ease with which it can be modified.

References

[1] E. W. Willihnganz, *Trans. Electr. Soc.*, **92** (1947) 281.
[2] F. G. Will and C. A. Knorr, *Z. Elektrochemie*, **64** (1960) 258.
[3] E. J. Ritchie, *J. Electrochem. Soc.*, **100** (1953) 53.
[4] A. Hyasahi and Y. Namura, *J. Jap. Tappi*, **21** (1967) 393.