JOURNAL OF APPLIED ELECTROCHEMISTRY 4 (1974) 351–356

Evaluation of expanders used in the negative lead battery electrode

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Received 11 March 1974

A method for studying the influence of expanders on the capacity of a thin layer of porous lead cathode is described. Acetylene black, $BaSO_4$, lignin, humic acid and two sorts of wood flour have been used. The mode of change of capacity and hydrogen evolution potential during cycling and the mean and initial capacities may be utilized for the characterization of the type of expander. The experiments show clearly that $BaSO_4$ crystals have an influence on the nucleation whereas the organic expander affects the growth of $PbSO_4$. Acetylene black increases the conductivity of the mixture.

1. Introduction

Expanders such as lamp black, barium sulphate, wood flour, and organic extracts of wood are added in small amounts to the paste for making negative plates, to prevent contraction and solidification of the spongy lead and the consequent loss of capacity and life of the finished battery [1]. The effect of $BaSO_4$ and lignin derivatives on low temperature, high-rate discharge capacity has been reported by Pierson and Gurlusky [2] Willihngunz [3], Ritchie [4], Zachlin [5], Popova and Kabanov [6], Barnes [7], Yampol'Skaya, and Kabanov [8], and Simon [9]. Recently Nickolas and Jakobjevich [10] and Brennan and Hampson [11] applied the voltammetric sweep method as a rapid tool for evaluating organic expanders; lead sheets, rods and wires were used. Since the role of an expander is to maintain the porous nature of the negative plate, a rapid method for the evaluation of these materials should be based on a porous electrode. The present paper describes a relatively rapid method which utilizes a reproducible thin layer of porous lead.

2. Experimental

The cell used in the present work is schematically shown in Fig. 1. The counter electrode was a lead plate. The potential was measured against $Hg/HgSO_4/SO_4^=$ via a luggin capillary, 1 mm from the electrode. A valve potentiometer (type E–353) Metrohm, Switzerland, was used to measure the potential. The current was kept constant with a constant-current device. The mixtures used had the following compositions (weight percentages): 90% lead oxide + 10% acetylene black (mix 1); mix 1 + 1% $BaSO_4$ (mix 2), 1% commercial lignin (Vanine) (mix 3) or 1% commercial humic acid (mix 4); mix 1 + 0·5% ply wood flour (mix 5), 0·5% cotton stalk flour (mix 6), 0·5% vanine (mix 7) or 0·5% humic acid (mix 8). The lead oxide containing 70% PbO and 30% Pb (Ball mill oxide), vanine and humic acid were provided by Egyptian Plastics and Electrical Industries. Half-gram quantities of the mixture were sandwiched between thin graphite layers and perforated lead discs, 5 cm in diameter.

The formation at the thin layer was conducted in $2N$ H_2SO_4 at 5 mA cm^{-2} for 6 h. The electrode assembly was then transferred to a glass vessel containing $10\,N$ H_2SO_4, the counter electrode and the luggin capillary.

Prior to each experiment the perforated lead disc was covered with pure pycene wax. The lower surface (diam. 5 cm) was cleaned with saturated ammonium acetate and then mechanically polished down with OO emery paper, and finally rubbed with a clean silk cloth.

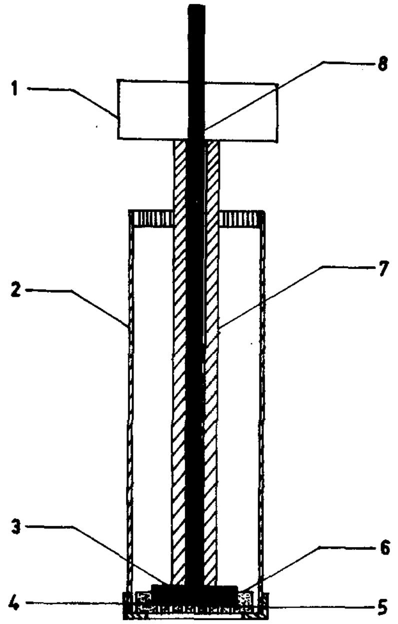

Fig. 1. Construction of electrodes. 1, weight (1·5 kg); 2, PVC cylinder; 3, perforated lead disc; 4, mixture; 5, filter paper; 6, perforated PVC disc; 7, PVC tube; 8, lead wire.

The assembled cell was then lowered to a fixed height. The electrodes were cycled at 5 mA cm^{-2}. When the step corresponding to the Pb/$PbSO_4$ couple was completed, the potential was reversed. Complete reduction of $PbSO_4$ formed anodically was indicated by a drop in potential to the hydrogen evolution values. After 1/2 h this value was recorded (hydrogen evolution potential) before reversing the current.

3. Results

3.1. *Plots of capacity against number of cycles*

Figs. 2 and 3 show plots of capacity against number of cycles for the different mixtures used (see Experimental). By capacity we mean the amount of charge consumed along the step corresponding to the oxidation of Pb to $PbSO_4$, at the end of which reversal of current was effected. The curve (Fig. 2, curve a) obtained for mix.1 (containing acetylene black only) displays pronounced fluctuations throughout its life. After 11 cycles the capacity drops to zero. For mix 2 ($BaSO_4$; the curve b) the capacity, after the first cycle, decreases linearly for another 7 cycles before it drops to zero. Curve c, Fig. 2 obtained for mix 3 (vanine) shows a drop from a comparatively high value, whereupon a more or less steady value is approached and nearly maintained for 11 cycles before fluctuations begin. The curve obtained for mix 4 (humic acid; curve d) shows that the capacity increases linearly along 6 cycles till a more or less steady value is reached. It is then maintained for 14 cycles; consequently fluctuations set in.

Fig. 3 shows the relevant curves obtained for the mixtures 5–8 containing $BaSO_4$ + organic expander. Curves a–c possess a nearly similar shape to that obtained for vanine alone. Fluctuations set in after 15, 17 and 18 cycles for mixtures 5, 6 and 7 respectively. The curve d obtained for mix 8 ($BaSO_4$ + humic acid) shows a novel feature, namely, a maximum at the third cycle. Furthermore the fluctuations manifested in the later stages start after 25 cycles and are preceded by a more or less gradual diminution in capacity.

The initial capacity amounts to 20–20·9mA–min for mix 1 for the mixtures containing humic acid (mixes 4 and 8) and to 46–47 mA-min for mixtures containing lignin (mixes 5–7). It is interesting to note that the maximum recorded for mix 8 amounts to 46 mA-min. The starting capacity pertaining to $BaSO_4$ is intermediate between the above values, namely 36 mA-min.

The steady state capacity is highest for mix 8, amounting to 32 mA-min. However, it amounts to 27 when humic acid is used alone (mix 4). The corresponding capacities measured for the mixtures containing lignin, range between 19 and 21 mA-min. Curve b, Fig. 2 obtained for mix 2 does not show a steady state. The fluctuations displayed by the rest of the curves occur about a mean value of about 18 mA-min.

3.2. *Plots of hydrogen evolution potential against number of cycles*

Figs. 4 and 5 illustrate the mode of change of hydrogen evolution potential during cycling. Curve a, Fig. 4 obtained for mix 1 shows an irregular tendency towards more negative values with the number of cycles. Curve b, on the other hand,

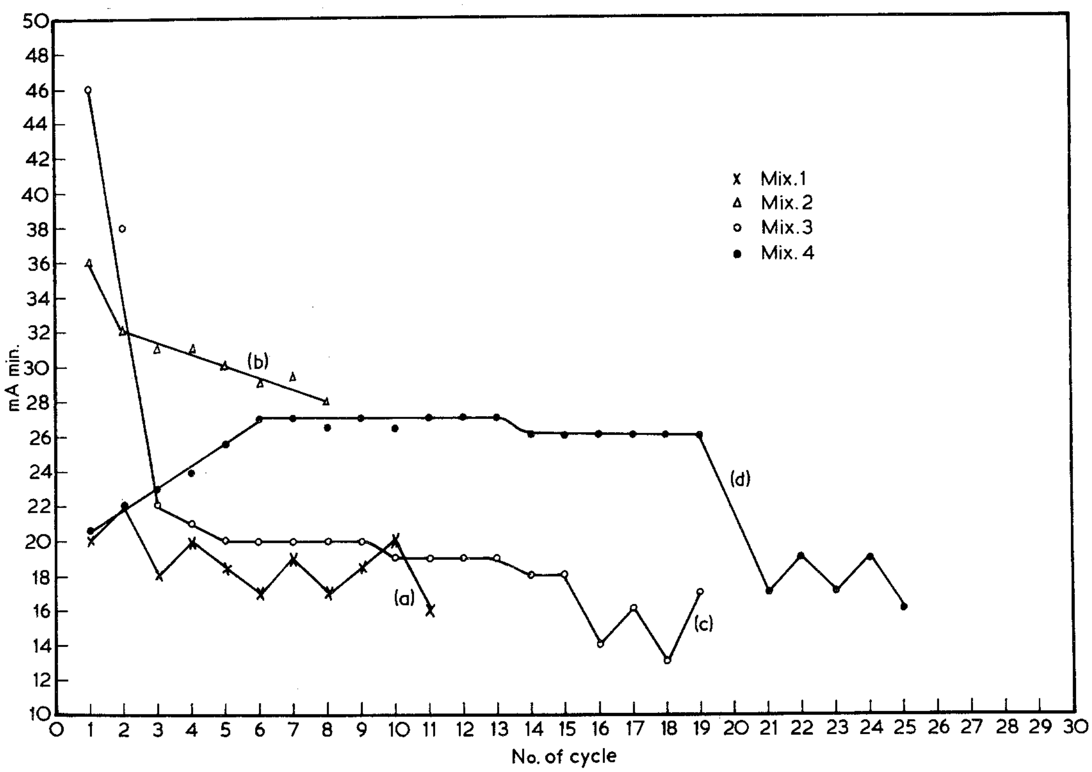

Fig. 2. Capacity against number of cycles for mixes 1–4.

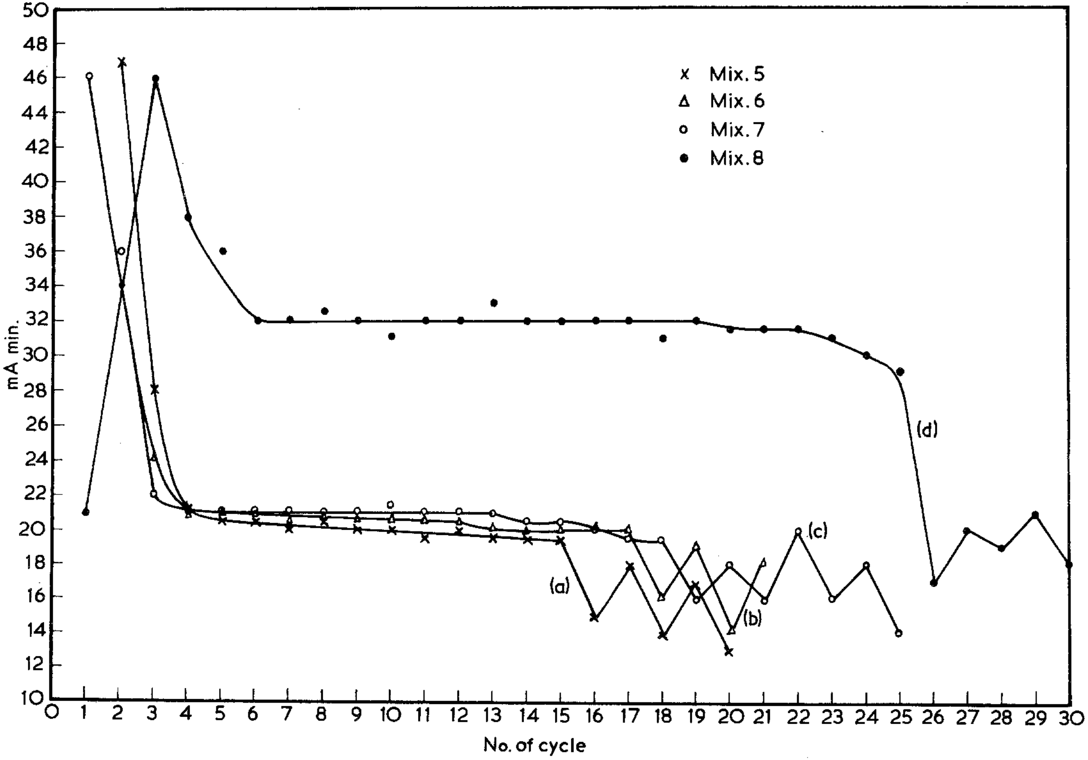

Fig. 3. Capacity against number of cycles for mixes 5–8.

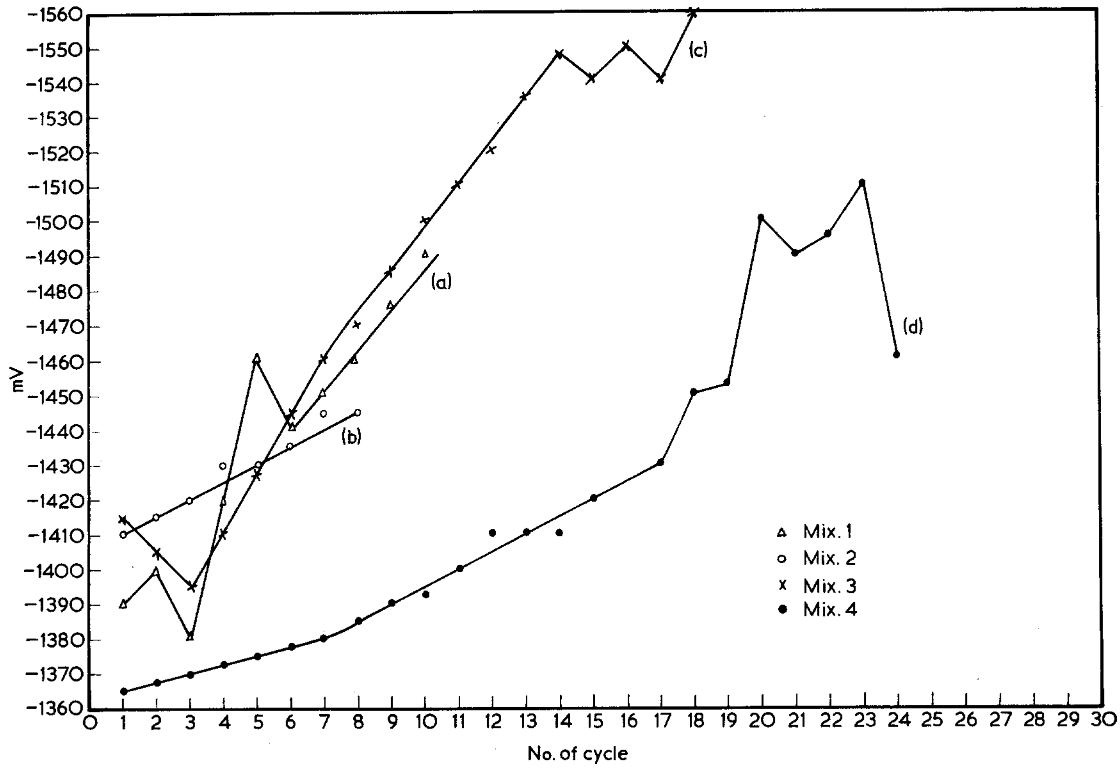

Fig. 4. The change of hydrogen evolution potential during cycling for mixes 1–4.

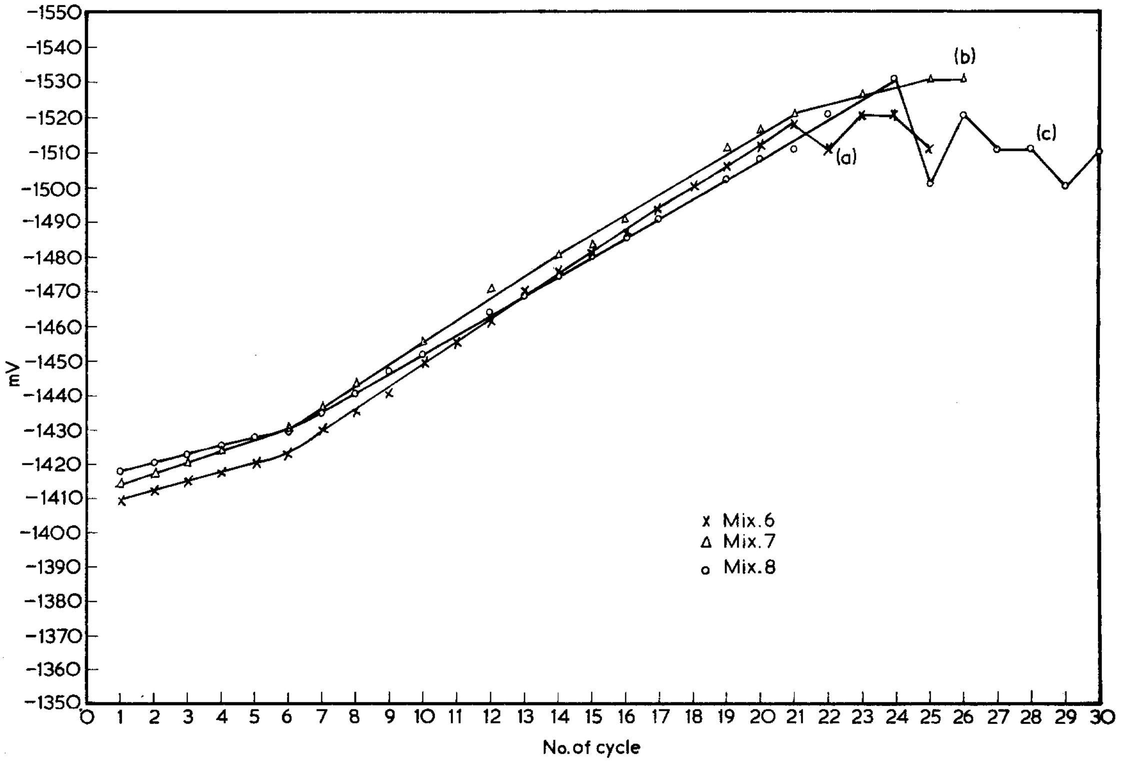

Fig. 5. The change of hydrogen evolution potential during cycling for mixes 5–8.

obtained for mix 2, reveals a linear decrease with number of cycles. When the mixture contains vanine (mix 3) the curve c shows an initial ennoblement, whereupon the potential decreases linearly with number of cycles, displaying a break at the seventh cycle. After 14 cycles the potential begins to fluctuate. Curve d shows two linear sections, the second one starting after the sixth cycle; pronounced fluctuations set in after the ninth. Curves a, b and c, Fig. 5 (mixes 6–8) offer the same picture although the curves are shifted in the negative direction by about 80 mV.

The slopes of the first and second linear sections amount, for mixes 4–8, to 2·6 ± 0·4 and 5·7 ± 0·7 mV per cycle respectively. The slopes of the corresponding curve measured for mix 3 are comparatively high.

4. Discussion

The pronounced fluctuations displayed by the two curves obtained for mix 1 (Figs. 2a and 4a) reveal a variation of the surface area exposed after each cycle. This irreproducibility may be the result of competition between initiation and growth of lead sulphate crystals formed electrochemically. The changes in the true surface area available for reduction of hydrogen ions will cause changes in true current density and hence in the hydrogen evolution potential.

It is generally agreed that $BaSO_4$ crystals act as nuclei when $PbSO_4$ is being formed. It probably favours initiation at least during the early cycles and prevents the formation of $PbSO_4$ film on the lead crystals. The immediate effectiveness of $BaSO_4$ [1] is evident from an increase in the initial capacity by about 80%. However, the early breakdown and the absence of fluctuation may be ascribed to the fact that $BaSO_4$ influences the rate of nucleation of $PbSO_4$ but not its rate of growth. The slow rate of increase of hydrogen overvoltage with cycling accords with the corresponding slow rate of decrease in capacity.

Consideration of the behaviour of mixes 3 and 4 shows that the two organic expanders have undergone electrolytic reduction or oxidation during the first cycles since the capacity of the former decreases and that of the latter increases before the steady-state capacity is attained. It has been suggested [2] that organic expanders adsorb on the growing faces of $PbSO_4$, enabling a more porous layer to be formed. The different effects brought about by the two inhibitors on the steady-state capacity and on the hydrogen overvoltage may be ascribed to different modes of action. The organic substance may adsorb uniformly on some crystal faces but not so much on others, selectively on the planes or preferentially on micro-peaks owing to greater diffusion of the organic substance to those peaks [12].

The continuous increase in hydrogen overvoltage within the horizontal section of the capacity curves obtained for mixes 3 and 4 may be correlated with a progressive adsorption of the organic substance on the lead surface [8, 13, 14]. The slow step in the reduction of hydrogen ions on the lead cathode is the discharge of these ions [15]. Adsorption of the organic expander may result in a decrease in the true surface area available for hydrogen deposition as is probably the case with humic acid (mix 4). Lignin may additionally distort the potential distribution in the phase boundary and hence increase the Tafel slope [16].

The appearance of fluctuations in capacity or potential prior to breakdown reveals the desorption of the organic expander or more probably the transformation to a non-effective form. The view that $BaSO_4$ and an organic expander are most effective when used together [2] is substantiated by the results of the present work. It is clearly shown that the influence of organic expander is complementary to that of $BaSO_4$. According to Archdale and Harrison [17] and Brennan and Hampson [11] the oxidation of lead in sulphuric acid could take place via a dissolution-precipitation process and a solid state reaction involving direct attack by the sulphate anion upon the lead surface. The results of the present work may be explained in the light of these findings. It may be assumed that the dissolution-precipitation process (nucleation from pollution) is affected by $BaSO_4$ crystals which act as nucleation centres. However, repeated cycling may result in the coverage of this expander with Pb. Organic inhibitors, on the other hand, may influence the discharge process by inhibiting the growth of $PbSO_4$ crystals including the solid state growth of these crystals [17]. The additive influence of the two expanders is demonstrated by the maximum displayed by the capacity curve of mix 8.

The almost identical hydrogen overvoltage-cycle curves obtained for lignin and humic acid in the presence of $BaSO_4$ suggest a similar mechanism for the combined expanders. However, the results lead to the important conclusion that, whereas the steady-state capacity depends on the type of expander, the number of cycles obtained, is a function of its quantity. Thus the steady-state capacity is almost identical for lignin obtained from three different sources. However, the number of cycles is highest for vanine and lowest for plywood. These results are in accord with the lignin-content in the three specimens; it amounts to 24–26% in cotton stalks and to 22·6% in plywood.

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