

# Electrochemical evaluation of additives for lead–acid batteries under high-discharge conditions

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## Abstract

Organic expanders play an important role in the lead–acid battery. This study presents the design of an electrochemical method which evaluates the influence of some commercial expanders on the performance of the negative plate. Examination is made of different commercial expander formulations which are prepared in the laboratory under carefully controlled conditions. In order to compare their influence on the behaviour of the negative plate, potential step and cyclic voltammetric techniques using high-potential polarization are performed. The results allow the selection of those expander additives which exert the best electrochemical effect on high-rate discharge reactions at negative plates. © 1999 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

The economics of lead–acid batteries have led to the search for a rapid and reliable method for the evaluation of the additives which are required in the negative plates of these batteries. The additives are called ‘expanders’ and their mechanism of action has been studied in detail by Pavlov [1]. It has been found that expanders of the ligno-sulfonate type are strongly adsorbed on the lead surface, and during lead dissolution the  $Pb^{2+}$  ions migrate through the adsorbed layer. This adsorption of the expander affects the anodic oxidation of Pb [2], the cathodic reduction of lead sulfate [3], the morphology of lead sulfate, and both the porosity and the surface area of the negative-plate material [4,5]. In particular, the presence of an expander restricts the crystal growth of the porous lead active material and, thereby, increases the active surface area of the negative plate [6,7]. The resulting small crystals are consumed during discharge and reformed during recharge [8].

The change in the porous structure of the plate due to expander adsorption reduces polarization during discharge, and improves negative-plate behaviour under high-current

discharge both at low temperatures and at high acid concentrations. In addition, expanders affect the hydrogen overpotential with consequent discharge inhibition.

The oxidation of lead to  $PbSO_4$  is a dissolution–precipitation process which is controlled by the diffusion of  $Pb^{2+}$  ions through the perm-selective  $PbSO_4$  layer [9]. Microscopic analysis suggests that electrochemical oxidation of lead in the presence of an expander produces a more porous  $PbSO_4$  layer with greater ionic permeability. Consequently, the diffusion of  $Pb^{2+}$  ions through such layer is favoured, as is the process of metal oxidation. Mahato [10] has suggested the possible formation of a  $Pb(II)$ –lignin complex, which ultimately causes precipitation of  $PbSO_4$ , and which increases the porosity of the solid membrane. The formation of such a complex implies the need to apply a greater overpotential in the presence of an expander to reduce  $PbSO_4$  to lead. Mahato also employed cyclic voltammetry (CV) to evaluate the influence of expanders on the behaviour of the negative electrode, and to demonstrate this influence after a given number of cycles with respect to initial capacity and electrode discharge reactions.

The use of an electrochemical technique to examine and explain the influence of an expander on the potential

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dynamic response of a lead–acid battery negative plate has been reported by Saakes et al. [11]. Saakes and van Duin [12] also developed a technique to select suitable expanders and inhibitors. This was based on potential-sweep measurements and galvanostatic impedance techniques, and it was shown that determination of impedance at constant current improves significantly the understanding of the physical process which takes place during discharge of a negative plate and, thereby, permits adequate selection of the best additive. Meanwhile, Hall and Wright [13] performed potential-step experiments to study the formation of  $\text{PbSO}_4$  in  $\text{H}_2\text{SO}_4$  at  $-18^\circ\text{C}$ , ‘with’ and ‘without’ expanders, and proposed a mechanism of expander action for the charge-transfer process. Finally, there have been several other investigations [14–16] in which potential-sweep methods have been employed to explain the influence of different expanders on the discharge capacity of the negative plate.

The scaling-up of results obtained by the above techniques is not always reliable because it does not consider the effect of scaling-up itself or a possible synergy among the components of the expander formulation. Data from small-electrode studies can change when scaled-up to the negative plates of a battery, and thus realistic conclusions can only be drawn by conducting experiments on plates themselves.

To date, there has been no methodology to allow preselection of possible additives that takes into account all the effects of expanders and that also allows reliable scale-up to production levels. Accordingly, this work presents a simple electrochemical method, which combines the techniques of CV and chronocoulometry (CC), to provide rapid selection of the expander with the best impact on negative-plate performance. The laboratory procedure demonstrates high reliability in scaling-up to production levels.

## 2. Experimental

The expander formulations are listed in Table 1. Their efficiency and performance were tested and compared by means of CV and CC. A miniplate (area:  $4.6\text{ cm}^2$ ; thickness 1.3–1.5 mm) with 2.4 g of active material was used as the working electrode. The grid alloy was lead–calcium.

Table 1  
Expander compositions

Compound	$\text{BaSO}_4$	Carbon	Lignin
Range (wt.%)	1.0–0.2	0.30–0.15	0.4–0.15
A	Low	Low	Low
B	High	Medium	High
C	Medium	High	High
D	High	Medium	High
E	Medium	High	Medium

Table 2

Paste formula	
Lead oxide (g)	100
Water (g)	14.3
Sulfuric acid, 1.400 relative density (g)	12.3
Fibre (g)	0.1
Expander according to formula	

In CV testing, three series of 50 cycles were performed between  $-1.250$  and  $-0.700\text{ V}$  at a sweep speed of  $20\text{ mV s}^{-1}$ .

All the tests were conducted at room temperature using a Potentiostat–Galvanostat EG&G PAR 273A fitted with an Options 92/96, EG&G Interface Power Booster, and a KEPCO Bioperational Amplifier model BOP 20-20M. This equipment allows studies up to 20 A and 20 V.

The paste formulation is given in Table 2. After curing and drying, formation was carried out in  $3.15\text{ M H}_2\text{SO}_4$  with a current density of  $3.25\text{ mA cm}^{-2}$  at  $0.3\text{ A h g}^{-1}$ . A final charge at  $3.25\text{ mA cm}^{-2}$  for 4 h was applied in  $4.7\text{ M H}_2\text{SO}_4$ .

The experimental cell had a capacity of 2 l and contained the working electrode, two auxiliary  $\text{PbO}_2$  electrodes (each with an area of  $174\text{ cm}^2$ ), and a  $\text{Hg}/\text{HgSO}_4$ ,  $\text{SO}_4^{2-}$  reference electrode. After each discharge, complete recharge of the miniplate was achieved by applying a constant current of  $3.25\text{ mA cm}^{-2}$  to 130% overcharge in  $4.7\text{ M H}_2\text{SO}_4$ .

The percentage utilization of negative active-material (NAM) was taken as a measure of the effect of a given expander on the negative-plate capacity for a given number of cycles. Cycling was continued until physical evidence of plate damage was observed, such as active material shedding or blisters on the surface.

## 3. Results and discussion

In chronocoulometric studies with a single potential step, measurements were made of the quantity of charge

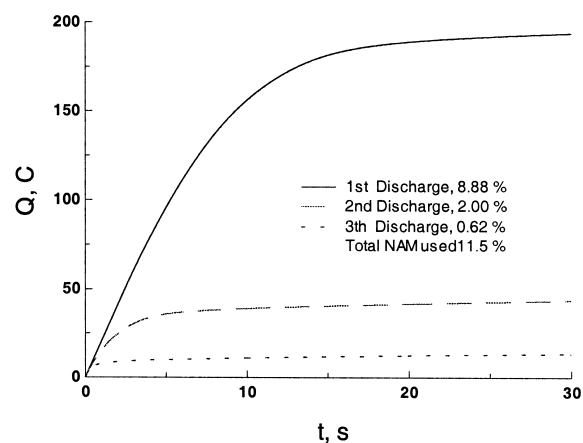


Fig. 1. Discharge transients of expander B under high polarization.

Table 3  
Percent NAM utilization in CC single-potential step

Expander	Cycle												
	1	2	3	4	5	6	7	8	9	10	11	12	13
A	24.20	22.77	22.58	18.40	21.65	14.94	15.34						
B	11.50	12.47	12.20	9.92	12.15	13.52	12.31	12.58	13.34	10.82			
C	14.20	9.64	11.18	8.71	7.72	7.38	7.45	6.79	6.77	6.49	6.63		
D	25.70	26.02	26.41	26.75	19.20	20.31	19.37	17.41	15.97	15.23	14.78	10.94	13.62
E	22.62	23.22	22.02	22.31	21.18	19.66	18.55	16.57	16.07	14.72	15.37		

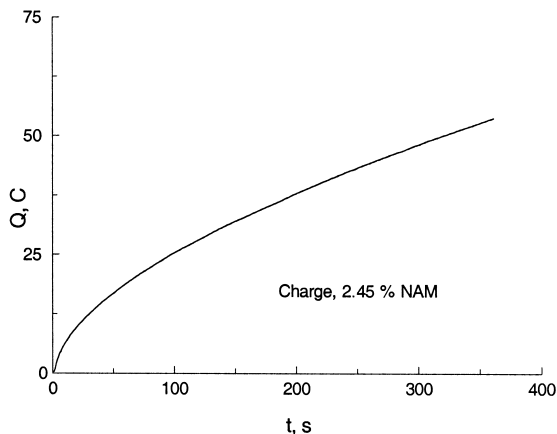


Fig. 2. Charge transient of expander B after high-polarization discharge.

which each plate with expander was able to produce during three successive discharges for 30 s, with a 30-min rest and no recharge between them, and when a potential step of 1.750 V was applied. The results for one type of expander (expander B) are presented in Fig. 1, and Table 3 summarizes the utilization of NAM for all the expanders. Once a plate was discharged, a potential of  $-1.350$  V was applied for 360 s and the quantity of charge accepted was measured. The charge transient for expander B is shown in Fig. 2. The utilization of NAM in three successive discharges under high polarization as a function of cycle number is listed in Table 3 for five expanders. The data reveal that increase in the number of discharges reduces the quantity of charge that a plate can deliver. Also, it is obvious that the best expander is D because it exhibits the highest utilization of NAM and withstands the greatest

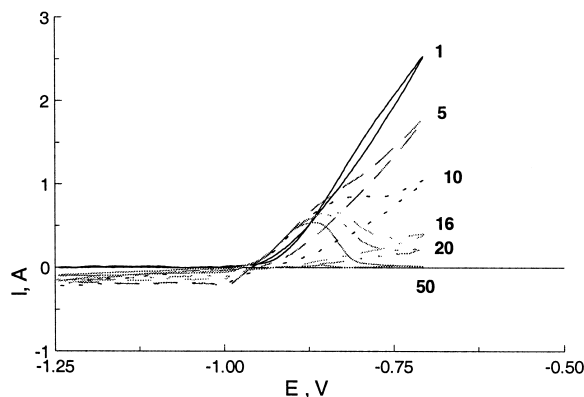


Fig. 3. Cycling effect on NAM utilization during test 1 of expander B.

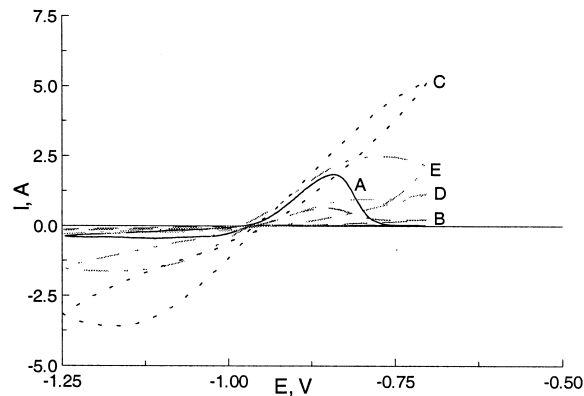


Fig. 4. Differences between expanders on test 1 at cycle 20.

number of cycles. By contrast, expander C displays the best recharging behaviour (Table 4), a finding which agrees with CV studies. These results are in accordance with the

Table 4  
Percent of charge recovery  $(Q_c/Q_d) \times 100$

Expander	Cycle												
	1	2	3	4	5	6	7	8	9	10	11	12	13
A	18.77	23.12	23.52	29.41	28.09	27.78	45.07						
B	21.36	29.3	27.46	32.74	28.35	27.54	30.13	34.2	26.85				
C	85.81	106.9	97.22	98.54	107.84	98.72	102.55	108.81	109.09	106.24	103.46		
D	17.43	23.83	17.87	20.15	21.33	29.22	25.84	25.81	31.09	36.02	44.44	49.68	38.75
E	56.56	59.4	69.58	70.77	75.19	75.32	71.82	78.04	81.22	84.38	89.5		

Table 5  
Percent NAM utilization during first and third test discharges in 50-cycle sequence

Cycle	Test	Expander				
		A	B	C	D	E
1	1	2.29	1.48	2.59	1.55	2.06
	3	2.59	1.79	2.77	2.12	3.32
5	1	1.20	1.10	2.75	1.35	1.65
	3	1.44	1.45	2.86	1.80	2.93
10	1	0.59	0.72	2.83	1.14	1.61
	3	0.74	0.87	2.95	1.47	2.89
16	1	0.51	0.39	2.85	0.94	1.61
	3	0.53	0.48	3.04	1.17	2.86
20	1	0.52	0.29	2.93	0.78	1.62
	3	0.53	0.40	3.08	0.97	2.91
50	1	0.61	0.15	3.02	0.21	1.85
	3	0.67	0.34	3.20	0.32	3.24

observation that an expander which favours high discharge also inhibits charge-acceptance.

Voltammograms reflect differences in behaviour of the miniplates with different expanders before recharging/discharging and during cycling. The CV analysis was made in terms of the quantity of charge that was obtained during cycles 1, 5, 10, 16, 20 and 50, both during recharge and discharge for the first and third test discharges. These results are reported in Figs. 3 and 4, and in Table 5. It is evident that expanders C and E display the best behaviour because they permit the negative plate to use the highest amount of NAM; the difference between them is quite small. This can be explained by the ready recharge of plates which contain these expanders; see Fig. 5.

The behaviour of all the expanders is given in Fig. 6 in terms of the percentage variation in the utilization of NAM during discharge between the first and third CV experiments at  $20 \text{ mV s}^{-1}$  for the selected cycles. The results demonstrate that expander E is the additive which experiences the greatest variation in NAM utilization. This expander promotes an increase in the volume of active material which, in turn, increases the reactive area of the negative plates. In effect, the plates become 'spongier'. This was confirmed by physical inspection: the plates developed blisters during cycling in the presence of the expander.

#### 4. Conclusions

The proposed electrochemical method, which consists of applying a combination of potential-step and potential-sweep techniques, offers a rapid and simple means to differentiate the impact of expanders on the performance of negative plates in lead-acid batteries. The resulting discharge and recharge transients show the effect of the expander on the electrode response under the current demand and charge-acceptance required during cycling.

The use of a miniplate as the electrode, and evaluation of the results in terms of the percentage utilization of NAM, provide a reliable method for selecting the most adequate expander before producing battery prototypes.

In future work, similar experiments will be performed at 40, 70, 0 and  $-18^\circ\text{C}$  in order to determine the chemical

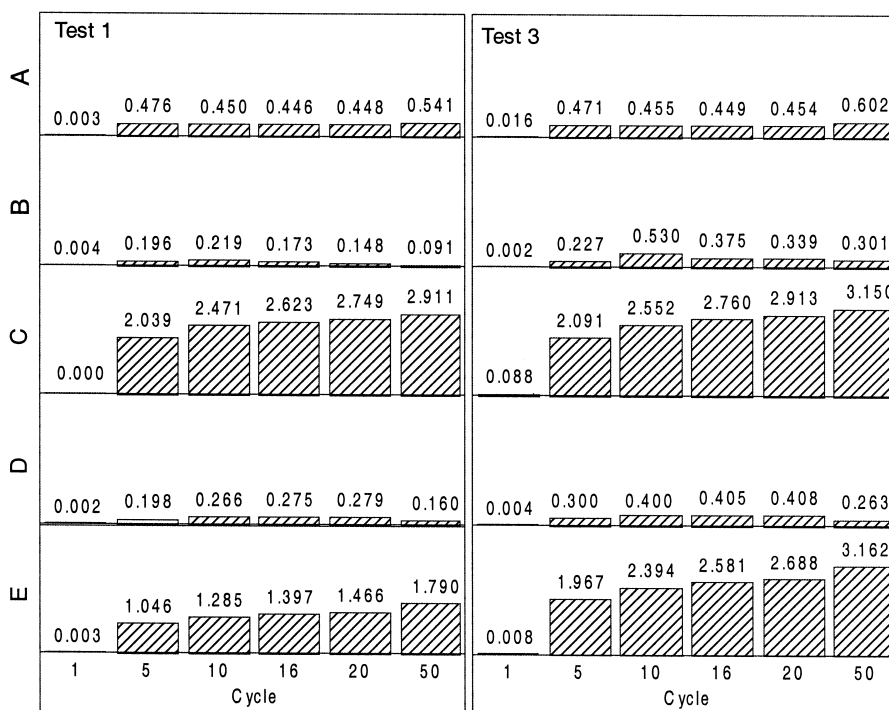


Fig. 5. Percent NAM utilization during discharge.

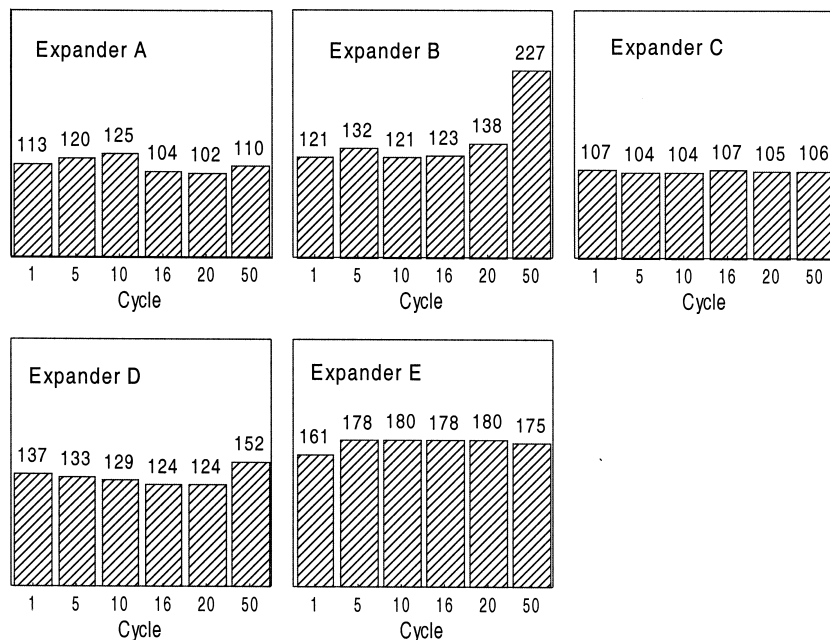


Fig. 6. Percent variation of NAM utilization between first and third series of cycles.

stability of the lignin component of the separator at different temperatures.

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