

A STUDY OF THE PREPARATION VARIABLES OF TUBULAR POSITIVE ELECTRODES FOR LEAD/ACID BATTERIES

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(Received December 17, 1984; in revised form February 7, 1985)

Summary

The effects, during formation, of current density, charge capacity, and concentration and temperature of H_2SO_4 electrolyte on the capacity of tubular electrodes in lead/acid batteries have been studied. Electrode capacity was found to be maximum at a H_2SO_4 concentration of 1.05 sp. gr., a charge amount of 250% theoretical capacity, a current density of $0.44 A dm^{-2}$, and an electrolyte temperature of $40^\circ C$. A study of the soaking process for tubular electrodes showed the electrode capacity to be maximum when the acid absorption was about 170 mg of H_2SO_4 per g of oxide. Finally, the discharge overpotential of tubular electrodes was analyzed by a galvanostatic transient method.

Introduction

The structure of the positive plate is the most vulnerable part of the traditional pasted-plate lead/acid battery. The capacity of the positive electrode decreases sharply during charge/discharge cycling as a result of both active material shedding and corrosion of the grid. The tubular electrode design provides better protection of the positive active material. The degree of shedding is reduced by enclosing the active material in a fabric gauntlet, and thus the cycle life of the battery is lengthened.

Tubular plate technology and performance characteristics have been the subject of much research. For example, Sundberg [1] investigated the impact of the shape of the tube on various electrochemical parameters; Voss [2] examined the effects of several variables on the formation; Rogatcher *et al.* [3] studied the correlation between the grid corrosion rate and both the thickness of active material and the charging current density; Lindholm [4] emphasized the importance of electrode design on the capacity; and Stevenson and Kuhn [5] investigated the effects of the packing density on the capacity and the cycle life. On the other hand, there has been little published information on the processes of soaking and formation of tubular

electrodes. For this reason, we have studied the soaking procedure of tubular electrodes and have attempted to determine the optimum conditions of formation.

Experimental

Tubular electrode preparation

Lead oxide powders were packed into a plate which consisted of three parallel, elliptical tubes with one end sealed. After packing, the other end of the tube was sealed and the electrode was soaked in 1.204 sp. gr. H_2SO_4 at 30 °C for 7 h. The tube was then removed from the H_2SO_4 solution and cured for five days at room temperature.

The cured, tubular, positive electrode was placed between two pasted, flat-plate negatives of similar size with separators in between. The capacity of the negative plates was considerably larger than that of the positive electrode so that the latter controlled the cell capacity.

Various conditions of formation were chosen. The concentration of H_2SO_4 electrolyte was varied from 1.01 to 1.20 sp. gr., the charging from 100% to 300% over the theoretical capacity, the current density from 0.37 A dm^{-2} to 0.73 A dm^{-2} , and the temperature from 20 °C to 60 °C.

After formation, 1.28 sp. gr. H_2SO_4 was used as electrolyte and the cell was charged for 12 h. The cell was then discharged at constant current until the voltage fell to 1.70 V. After discharging, the cell was recharged with a charge factor of 120%.

Pasted electrodes were supplied from the local Pilot Battery Co. for comparison purposes.

X-ray diffraction analysis

The composition and polymorphism of the various lead compounds in the electrode were determined by an X-ray diffraction (XRD) method using a cobalt target, a 4° min^{-1} scanning rate, and a 2θ range of 15 - 63°.

Galvanostatic transient measurements

A galvanostatic transient method was used to study the tubular electrode potential. The circuit diagram is shown in Fig. 1. A differential amplifier (Tektronix 5103 N with plug-in 5A 22N differential Ampl) was used to overcome the noise signal due to the IR resistance between the reference and the working electrodes. Accurate readings of ohmic drop, activation overpotential, and concentration overpotential were recorded on an oscilloscope.

Results and discussion

Packing density of lead oxide powder

The packing density of lead oxide powder affects the porosity and surface area as well as the stability of active material. Consequently, the

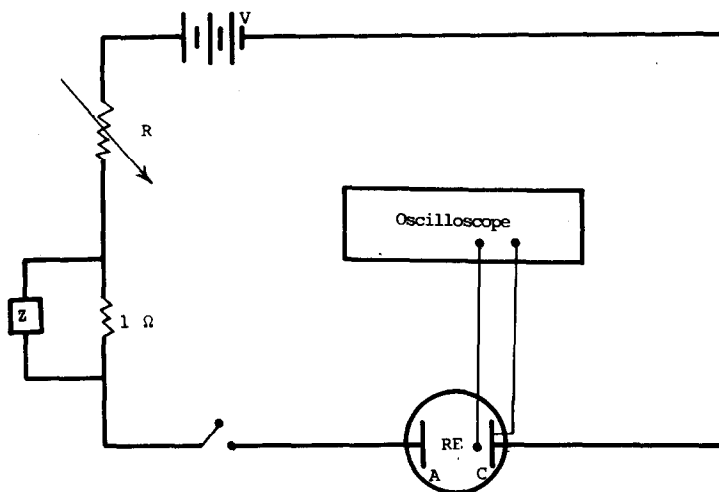


Fig. 1. Schematic of circuit for measuring electrode overpotential. A, anode of test cell; C, cathode of test cell; RE, reference electrode of test cell; R, variable resistance; V, 24 V, 240 A h lead/acid battery; Z, recorder.

active material utilization and the battery cycle life are greatly influenced by the packing density.

Packing densities in the range $3.47 - 5.45 \text{ g cm}^{-3}$ were prepared to examine the relationship between this parameter and the electrode capacity. The data presented in Fig. 2 show that the capacity initially increases with packing density and then reaches a limiting value ($\sim 7.5 \text{ A h}$). This is because, at a very high value of the packing density, the increased resistance to diffusion of H_2SO_4 into the electrode results in decreased utilization of active material.

The relationship between the packing density and the energy density of the electrode is shown in Fig. 3. It can be seen that the optimum energy density is attained when the packing density is about 4.38 g cm^{-3} .

Soaking process

Soaking is defined as the process of generating various lead sulphate compounds by the interaction of lead oxide powder and sulphuric acid when the packed tubular electrode is dipped into a solution of appropriate concentration. The process is similar to that of mixing/pasting in the traditional pasted-plate operation. However, the basic lead sulphates generated by these two processes are different. This is confirmed by comparing the XRD results presented in Fig. 4. The phase composition of the tubular and pasted electrodes can be determined using the XRD method developed by Hill [6]. The results are summarized in Table 1.

The marked increase of PbSO_4 for the tubular electrode in contrast to that of the pasted electrode is consistent with Kuhn and Stevenson's finding [7]. However, the low value of the PbO content in the pasted electrodes could be due to faulty operation in the paste mixing and curing stages, although the plates showed normal discharge performances after formation.

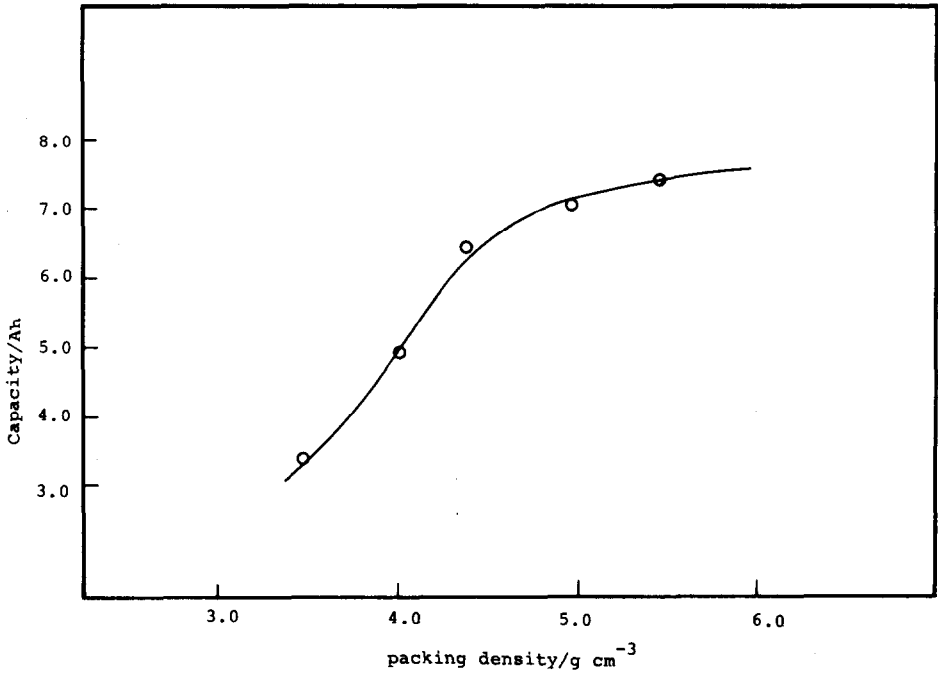


Fig. 2. Relationship between capacity and packing density of a tubular positive electrode.

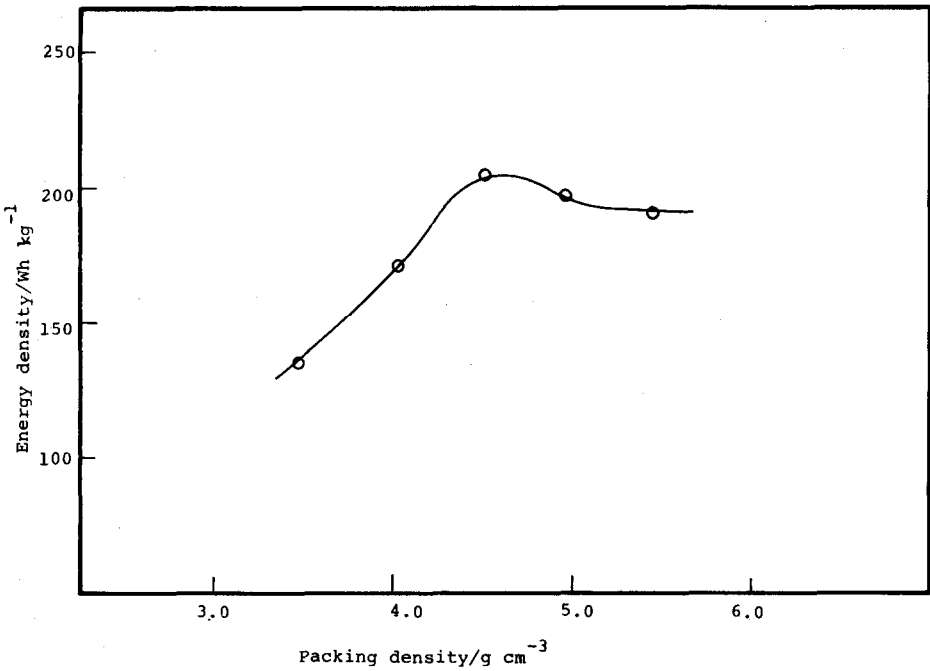


Fig. 3. Relationship between energy density and packing density of a tubular positive electrode.

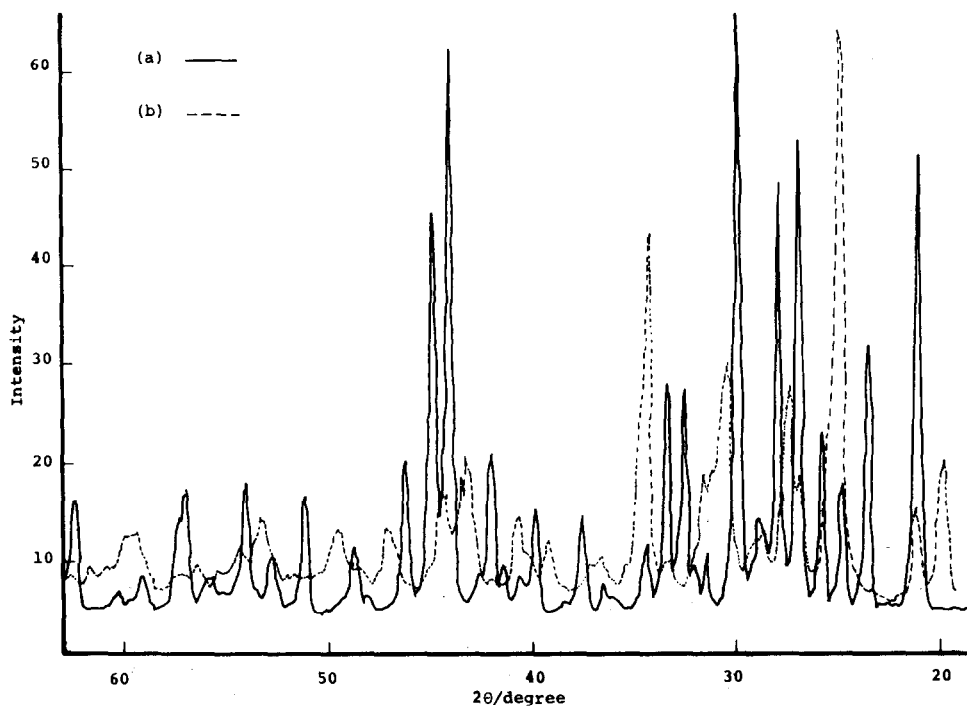


Fig. 4. X-ray diffraction pattern of (a) cured, tubular positive electrode, and (b) cured, flat-plate positive electrode.

TABLE 1

Composition of tubular electrode after soaking, and pasted-plate electrode after curing (wt.%)

Phase	Tubular electrode	Pasted-plate electrode
α -PbO	2.39	6.97
β -PbO	0.74	—
PbSO ₄	89.30	33.91
PbO·PbSO ₄	2.53	39.27
2PbO·PbSO ₄	5.04	19.84

Previous workers [3 - 5, 8] have shown that several factors, such as the length of soaking interval and the concentration of H₂SO₄, have significant influences on the capacity of the electrode. To better understand the effect of the H₂SO₄ concentration on the soaking process, tubular electrodes were soaked in H₂SO₄ of different concentrations for 7 h. Figure 5 illustrates the relationship between the acid concentration and both the acid absorption of lead oxide and the discharge capacity. It can be seen that as the concentration of H₂SO₄ increases, the acid absorption increases from 96.8 to 219.5 mg of H₂SO₄ per g of oxide. The electrode capacity reaches a maximum when the H₂SO₄ concentration is at about 1.2 g cm⁻³. In other words, both over-

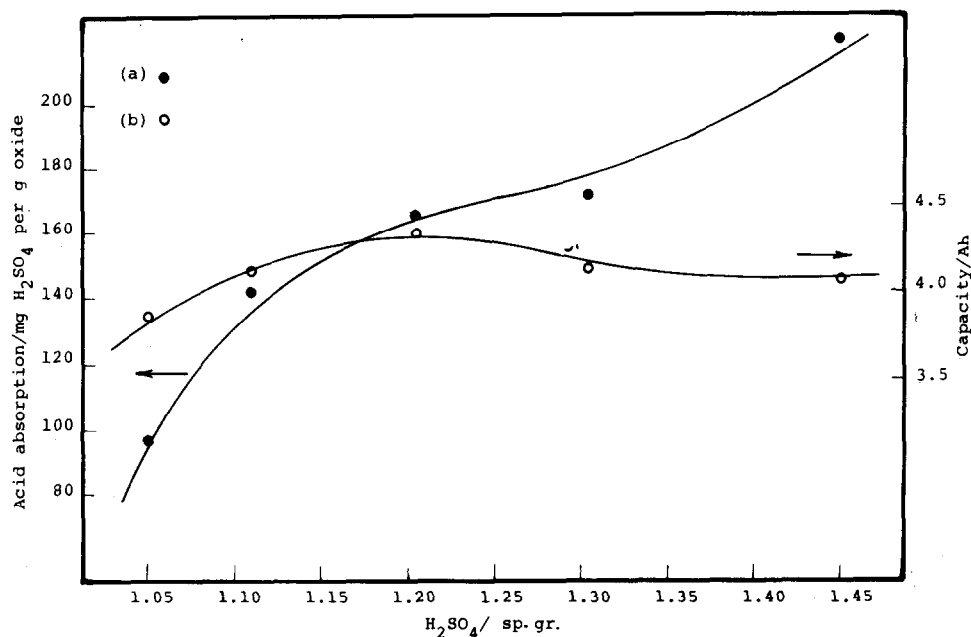


Fig. 5. Relationship between (a) acid absorption and (b) capacity and H_2SO_4 concentration; tubular positive electrodes dipped in H_2SO_4 for 7 h.

absorption and insufficient absorption of H_2SO_4 adversely affect the electrode capacity.

The $PbSO_4$ content after 7 h of soaking and the $\alpha + \beta-PbO_2$ content after formation were determined using XRD analysis [6] and wet chemistry titration [9]. The results, presented in Table 2, show that the amount of $PbSO_4$ formed increases as the concentration of H_2SO_4 increases. Since $PbSO_4$ has a higher oxidation potential than the basic lead sulphate compounds [10], the soaking of a tubular electrode in a higher concentration of H_2SO_4 will cause an increase in its oxidation potential. Correspondingly, the content of PbO_2 after formation decreases (Table 2).

TABLE 2

$PbSO_4$ content (wt.%) after soaking (7 h) and $\alpha + \beta-PbO_2$ content (wt.%) after formation in a tubular electrode

H_2SO_4 (sp. gr.)	$PbSO_4$ content after soaking	$\alpha + \beta-PbO_2$ content after formation
1.110	24.46	50.47
1.204	65.52	58.35
1.304	72.20	56.56
1.450	89.30	51.76

It was also found that when the tubular electrode was soaked in 1.11 sp. gr. H_2SO_4 , there was insufficient PbO_2 formed, despite the low content of PbSO_4 . X-ray diffraction analysis revealed that a large amount of the lead oxide remained unchanged after soaking. This accounts for its poor formation performance.

Figure 6(a) shows that when the tubular electrode was soaked in 1.40 sp. gr. H_2SO_4 , the acid absorption of the electrode increased with the duration of the soaking interval. The optimal electrode capacity was obtained when the electrode was soaked for 3 h (Fig. 6(b)).

Summarizing the results of Figs. 5 and 6, we conclude that the content of PbO_2 in the electrode is at an optimum value when the acid absorption is controlled at about 170 mg of H_2SO_4 per g of oxide (Fig. 7). In other words, one can maximize the electrode capacity by increasing either the length of soaking time or the concentration of H_2SO_4 so that the acid absorption reaches about 170 mg of H_2SO_4 per g of oxide.

Formation electrolyte

Figure 8 shows the relationship between the electrode capacity and the concentration of H_2SO_4 used during formation. Maximum capacity is achieved when the formation is carried out with H_2SO_4 of 1.05 sp. gr. A higher concentration will be deleterious to formation due to the difficulty in releasing SO_4^{2-} and H^+ ions in concentrated electrolyte [11]. On the other hand, the electrode capacity decreases if the concentration of H_2SO_4 is

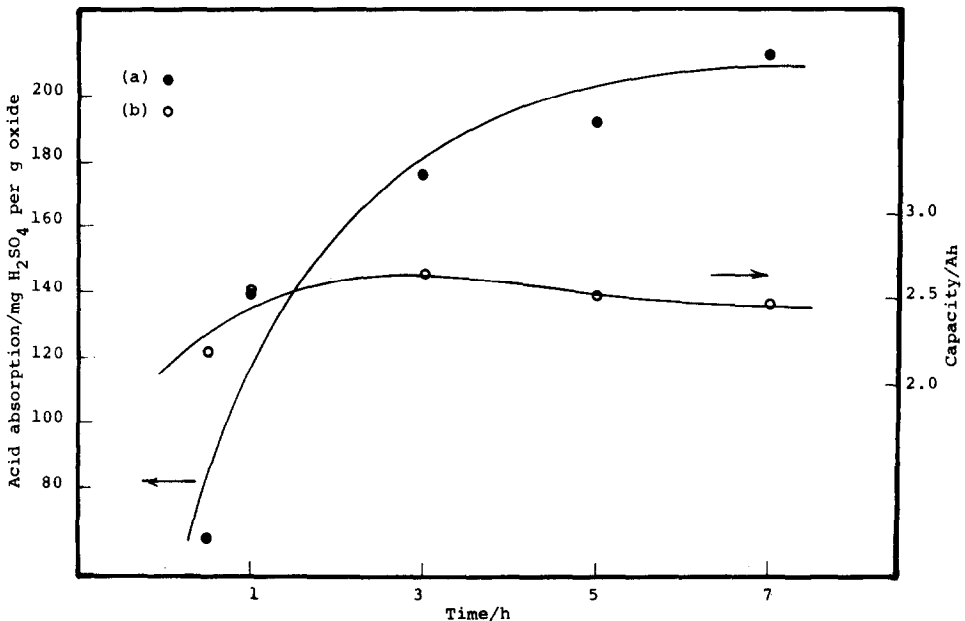


Fig. 6. Relationship between (a) acid absorption and (b) capacity and soaking time for a tubular positive electrode in 1.40 sp. gr. H_2SO_4 .

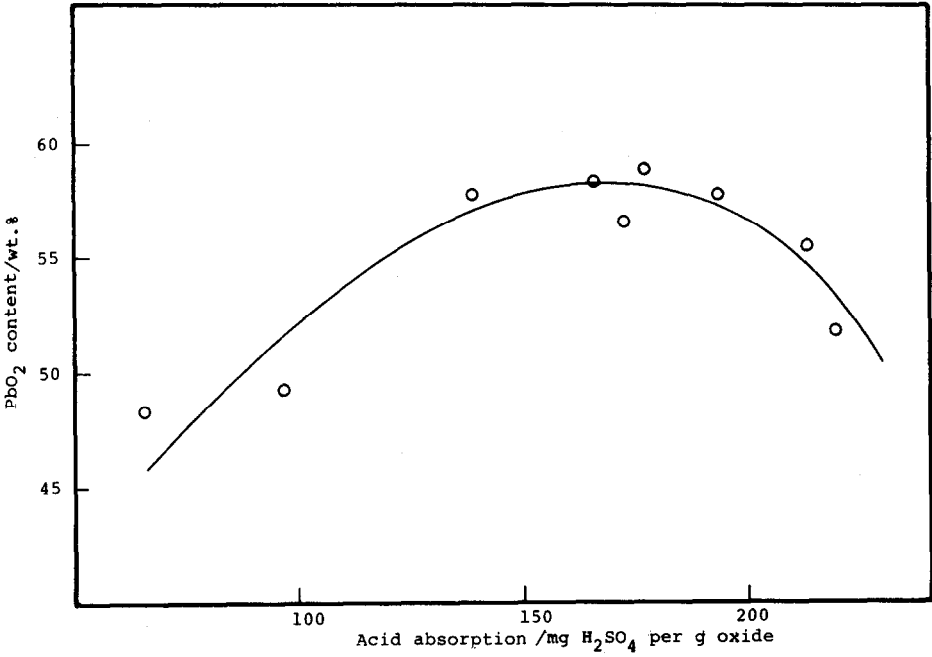


Fig. 7. Relationship between PbO₂ content of a tubular positive electrode and acid absorption after formation.

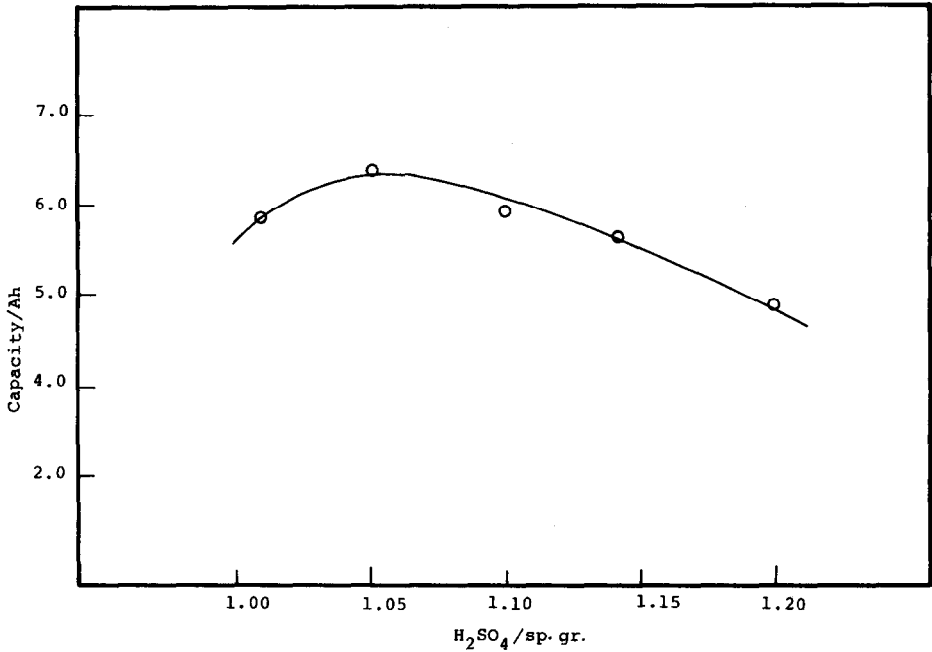


Fig. 8. Relationship between capacity and formation acid concentration of a tubular positive electrode.

too low. This is because the conductivity of the electrolyte is low and the charge efficiency decreases accordingly.

Formation temperature

Figure 9 shows that optimal electrode capacity is obtained when the formation temperature is between 40 and 50 °C. This finding is in agreement with that of Stevenson and Kuhn [5]. The conductivity of H₂SO₄ decreases at lower temperature and, consequently, the electrode capacity decreases.

Although the use of a higher formation temperature improves the conductivity of the electrolyte, there is an adverse effect on the structure of the active material. For example, shedding of active material was visible after several charge/discharge cycles in electrodes formed above 60 °C.

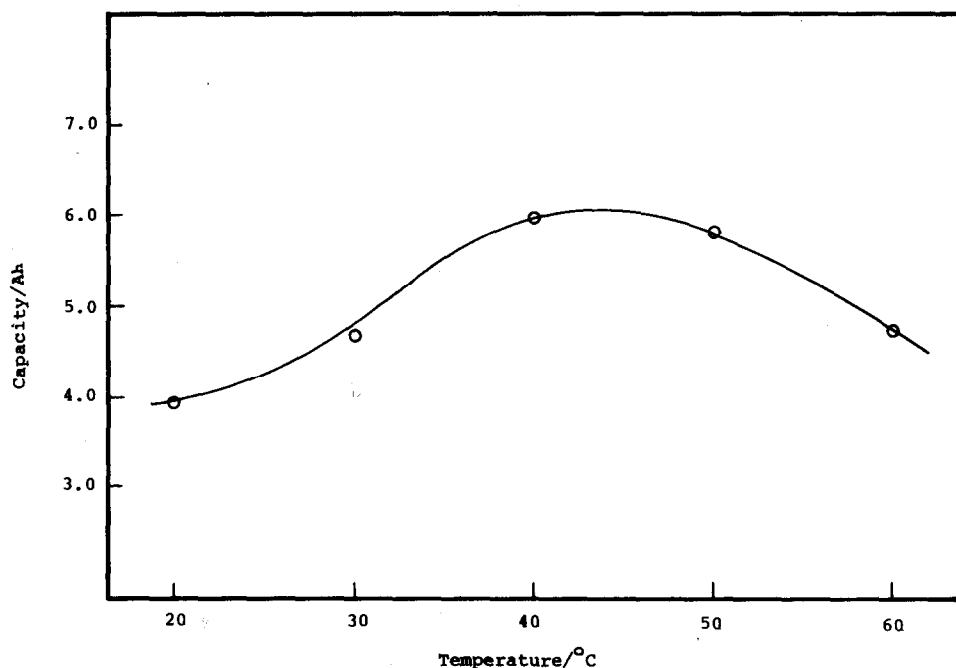


Fig. 9. Relationship between capacity and formation temperature of a tubular positive electrode.

Formation current density

The relationship between electrode capacity and current density is shown in Fig. 10 and Table 3. It can be seen that the current density has a negligible influence on the electrode capacity: the capacity increases from 0.37 to 0.44 A dm⁻² and then decreases. A possible explanation is that increased formation current density would result in a higher proportion of β-PbO₂ which has a higher surface area (9.53 m² g⁻¹) than that of α-PbO₂ (0.48 m² g⁻¹) [12, 13]. When the current density was increased further (above 0.44 A dm⁻²), the electrolysis of H₂O became significant and,

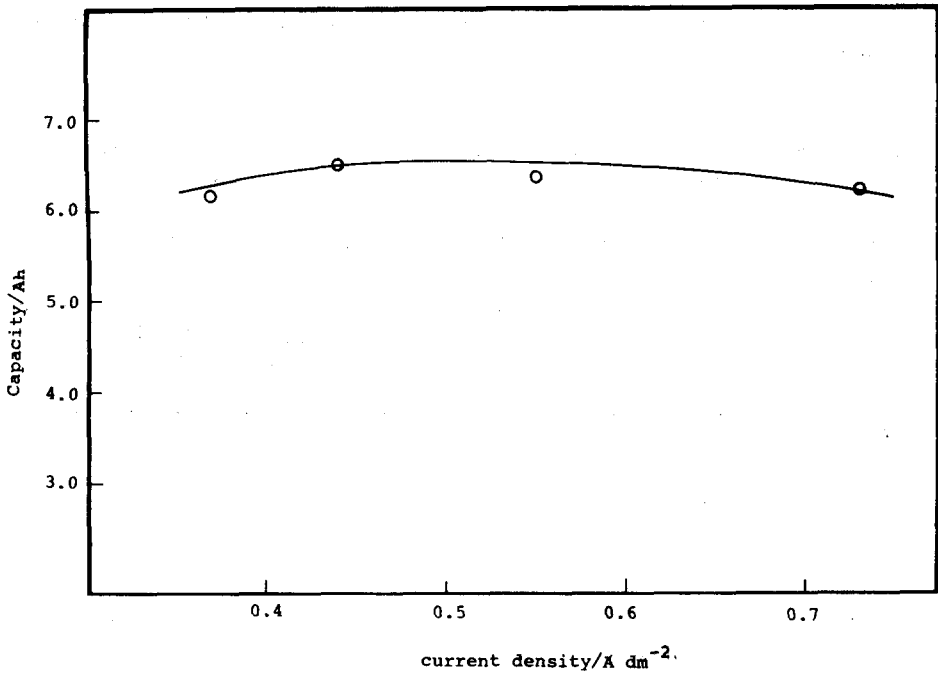


Fig. 10. Relationship between capacity and formation current density of a tubular positive electrode.

TABLE 3

PbO₂ and β-PbO₂ content (wt.%) of a tubular electrode at different formation current densities

Current density (A dm ⁻²)	PbO ₂ content	β-PbO ₂ /total PbO ₂
0.73	55.85	95.99
0.55	56.05	95.12
0.44	57.87	93.82
0.37	58.13	92.35

consequently, the content of PbO₂ and the electrode capacity both decreased.

Formation charge

Figure 11 shows that the electrode capacity passes through a maximum with increase in the amount of formation charge. The initial increase results from an increase in PbO₂ conversion. The eventual loss of capacity may be due to the fact that the excess charging will electrolyze H₂O and produce gas bubbles, which dislodge the active material from the electrode [5]. Consequently, the charge efficiency, as well as the electrode capacity, decreases.

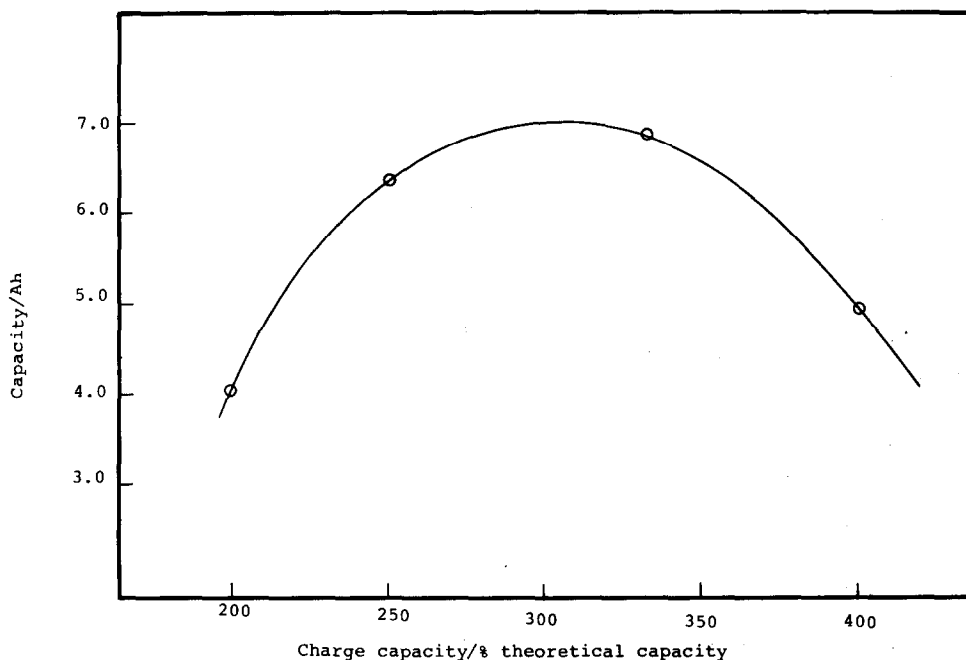


Fig. 11. Relationship between capacity and formation charge capacity of a tubular positive electrode.

Analysis of discharge overpotential

A galvanostatic transient method has been successfully used by the authors [14] to analyze the anodic overpotential of a redox battery. In the present work, this method was applied to the study of the discharge overpotential of a tubular lead/acid electrode. Figure 12 shows typical transient discharge curves for a tubular electrode. When the discharge current was increased, the overpotential naturally increased. However, a closer analysis of the overpotential showed that the concentration overpotential (η_{conc}) did not vary significantly, and that only the IR drop and the activation overpotential (η_{act}) increased as the current density was increased.

It was further found that the presence of a tube only affected the activation overpotential; this overpotential was about 20% higher for an electrode with a tube. (Note, the electrode could retain its physical integrity without a tube during measurement.) Whether this is because the partial shielding of the electrode by the tube causes uneven current distribution requires further investigation.

When the activation overpotential is smaller than 20 mV, the Butler-Volmer equation is reduced to:

$$i = i_0 \frac{nF}{RT} \eta_{act} \quad (1)$$

where i is the current density and i_0 is the exchange current density. From Fig. 13, the exchange current density for the tubular electrode is found to

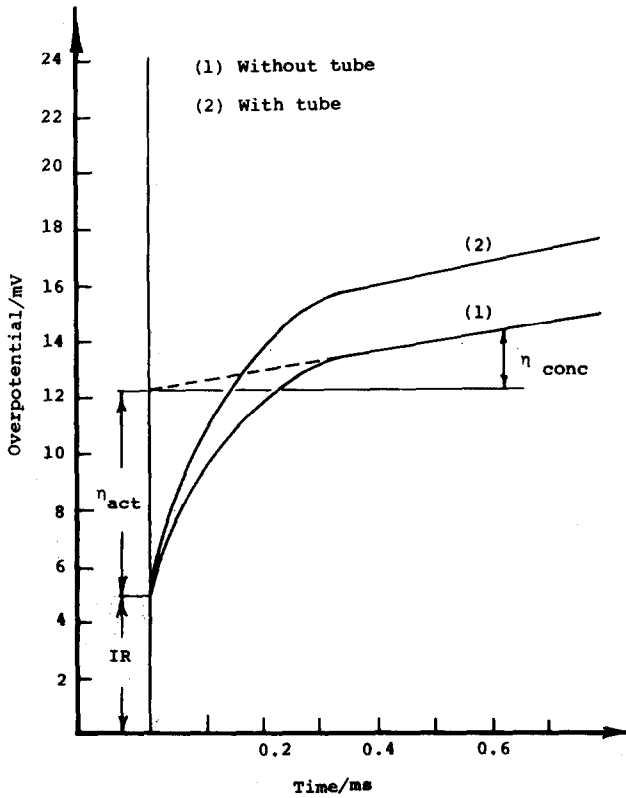


Fig. 12. Discharge curve for a tubular positive electrode: (1) without tube; (2) with tube.

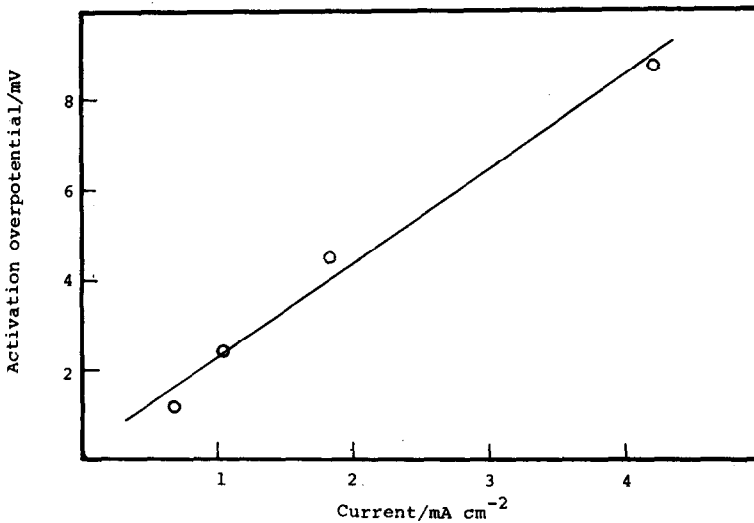


Fig. 13. Relationship between activation overpotential and discharge current density of a tubular positive electrode.

be $i_0 = 6.19 \text{ mA cm}^{-2}$. This value differs slightly from that found for a pasted-plate electrode using a Faradaic impedance method (32 mA cm^{-2} in $10\text{N H}_2\text{SO}_4$) [15].

Conclusions

From the studies reported in this paper, we conclude that:

(i) The packing density of lead oxide powder in tubular electrodes has a significant impact on the electrode capacity. The optimum packing density is about 4.38 g cm^{-3} .

(ii) The acid absorption and composition of the electrode are a function of the soaking time and H_2SO_4 concentration. The electrode capacity is maximum when the acid absorption is about 170 mg of H_2SO_4 per g of oxide.

(iii) A low concentration of electrolyte during formation is favorable for electrode capacity. The optimum concentration of H_2SO_4 is about 1.05 specific gravity.

(iv) The electrolyte temperature during formation has a significant influence on electrode capacity. The optimum temperature is about 40°C .

(v) The electrode capacity is not very sensitive to the current density of formation under constant formation charge. The optimum current density is about 0.44 A dm^{-2} .

(vi) The optimum formation charge is between 250 and 330% of theoretical capacity. To avoid overcharge, 250% of theoretical capacity is preferred.

References

- 1 E. Sundberg, *Proc. Second Int. Conf. Lead*, Pergamon Press, Oxford, 1967, p. 227.
- 2 E. Voss, *J. Power Sources*, 7 (1982) 343.
- 3 T. Rogatchev, G. Papazov and D. Pavlov, *J. Power Sources*, 10 (1983) 291.
- 4 A. S. M. Lindholm, *J. Power Sources*, 10 (1983) 71.
- 5 J. M. Stevenson and A. T. Kuhn, *J. Power Sources*, 8 (1982) 385.
- 6 R. J. Hill, *J. Power Sources*, 9 (1983) 55.
- 7 A. T. Kuhn and J. M. Stevenson, *J. Power Sources*, 10 (1983) 389.
- 8 M. Barak, in M. Barak (ed.), *Electrochemical Power Sources*, Inst. Electr. Eng., New York, 1980, p. 269.
- 9 M. Denby, in D. H. Collins (ed.), *Batteries*, Pergamon Press, New York, 1963, p. 439.
- 10 D. Pavlov, G. Papazov and V. Iliev, *J. Electrochem. Soc.*, 119 (1972) 8.
- 11 M. Denby, in D. H. Collins (ed.), *Batteries*, Pergamon Press, New York, 1963, p. 243.
- 12 P. Reutschi and B. D. Cahan, *J. Electrochem. Soc.*, 105 (1958) 369.
- 13 P. Ruetschi and R. T. Angstadt, *J. Electrochem. Soc.*, 111 (1964) 1323.
- 14 Y. Y. Wang, M. R. Lin and C. C. Wan, *J. Power Sources*, 13 (1984) 65.
- 15 E. Y. Weissman, in K. V. Kordesch (ed.), *Batteries*, Vol. 2, Marcel Dekker, New York, 1977, p. 5.