

## THE ROLE OF ADDITIVES IN THE POSITIVE ACTIVE MASS OF THE LEAD/ACID CELL

S. V. BAKER, P. T. MOSELEY\* and A. D. TURNER

*Materials Development Division, Harwell Laboratory, Oxfordshire OX11 0RA (U.K.)*

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### Summary

Lead-acid cells have been assembled with tubular positive plates containing chemically prepared  $PbO_2$  admixed with a small mass fraction of second phase material. The manner in which graphite, in particular, affects the initial discharge capacity of cells prepared in this way has been examined. It has been shown that in addition to its influence on porosity and diffusive mass transport in the cell, the possibility that an additive gives rise to electro-osmotic pumping must be considered where the material added has a high zeta potential.

Electro-osmotic pumping offers a means to improve the performance of lead-acid battery plates regardless of the method used to prepare them.

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### Introduction

Arising from the perception that massive new markets, particularly in the field of transportation, await the development of a battery offering a high energy density combined with long life, there has been worldwide effort, over the past 15 - 20 years, to develop new types of secondary energy storage devices. None of the proposed new systems is yet on the point of commercial exploitation and the lead-acid battery, notwithstanding the limitation imposed by the specific gravity of lead and its compounds, remains the only principal for most applications requiring a substantial rechargeable power supply.

Despite this dominant position and the antiquity of the concept of the lead-acid cell, the technology of the battery continues to evolve. The lead-acid battery industry is highly competitive and so there is an incentive not only to raise the operating performance of the system in an attempt to reach such new markets as may develop, but also to achieve every possible economy in manufacture.

Significant advances made in recent years include system design changes such as the substitution of polypropylene for hard rubber in cell case con-

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\* Author to whom correspondence should be addressed.

struction with a consequent improvement in gravimetric energy density. At the same time, however, it has been re-emphasised [1] that new progress can also be greatly aided by the development of a deeper understanding of the function of the active materials in the cell, and the mechanism by which cell output falls over a period of time. There has been a resurgence of fundamental studies, of the active mass in particular, that have drawn on a powerful array of newly developed techniques.

The function of the positive active mass has been the focus of so much attention because it has been the least efficient component as well as the least well understood. At normal discharge rates most lead-acid positive plates yield much less than half their theoretical capacity and their performance falls progressively over most of their lives. Several mechanisms, including the development of a barrier grid corrosion film, active material encapsulation, and active material shedding, have been proposed to account for the loss of capacity, and one theory involving an electrochemically inactive form of  $\text{PbO}_2$  (to which the "active" form was thought progressively to convert) was linked to the proposal that  $\text{PbO}_2$  prepared by a chemical method would be incapable of yielding a discharge. A corollary of this theory would be that the present electrochemical batch process for positive plate manufacture is unavoidable. The proposed role of hydrogen species and crystalline interfaces [2] have been investigated with the aid of neutron [3, 4] and electron microscope [5] techniques, respectively, and it has now been shown [6 - 8] that the inactivity of chemically prepared  $\text{PbO}_2$  is a myth. Plates made with such materials have been shown to achieve at least comparable levels of capacity with those of conventional plates [6]. It is thus possible to consider alternative (possibly more economic) methods of plate manufacture, and to investigate new ways of improving on the presently low levels of utilization of active material.

The major limitations on the performance of the lead-acid battery are the initial discharge capacity obtainable from the positive plate and the degradation processes by which the available capacity declines. Attempts to improve capacity by altering dimensions or microstructure have generally involved a trade-off in terms of reduced cycle life. Efforts to overcome this problem by the incorporation of additives within the positive active mass have met with some success. The use of particles of anisotropic graphite greater than  $2 \mu\text{m}$  in pasted plates has been reported [9] to provide significant increases in utilisation of active material. In this cell the beneficial effect of the additive is attributed to a mechanism of porosity enhancement and, hence, of improved mass transport in the positive active mass.

There are clearly several ways in which second phase particles might modify the discharge characteristics of lead dioxide cathodes:

(i) Maintaining an electrically conducting path to all parts of the active mass as the conversion from conducting  $\text{PbO}_2$  to insulating  $\text{PbSO}_4$  proceeds.

(ii) Provision of microporosity to 'wick' electrolyte into the positive active mass and keep it irrigated despite gassing.

(iii) Oxidation (in the case of graphite) to form gas phase products ( $\text{CO}_2$ ) which could expel electrolyte.

(iv) Surfactant role to maintain good wetting by the electrolyte.

(v) Pore formation following removal by processes such as (iii) above.

(vi) Electro-osmotic pumping which would, depending on the sign of the zeta potential of the solid components, be capable of encouraging the flow of acid either into, or out of, the positive plate during discharge.

This paper describes the incorporation of some additives in tubular positive plates (as distinct from the flat plates used in ref. 9) containing chemically prepared  $\text{PbO}_2$  and, in particular, investigates the role that electro-osmotic pumping might have to play in affecting the discharge capacity of the lead-acid cell.

## Materials and experiments

Tubular positive plates were used as a convenient means of mixing additives and lead dioxide powder without the need to incorporate any third material solely to provide adhesion or to go through curing and formation stages before test. Cell components used in this work were those manufactured for a 13 A h miner's cap battery with a tubular positive and a flat negative plate, and were kindly supplied by Oldham Batteries.

Lead dioxide was prepared by treating  $\text{Pb}_3\text{O}_4$  with nitric acid, washing, and filtering, as described earlier [6].

Electrodes were prepared from the "chemical"  $\text{PbO}_2$  by mixing it with varying proportions of an 8  $\mu\text{m}$  synthetic graphite (Rocal foliac graphite, X7160 grade) and compacting the material mechanically. The loss of active material through the walls of the electrode tubes, identified in early experiments, was overcome by inserting inner liners of microporous polypropylene sheet, supplied by Tullis Russel & Co. Ltd., into the tubes.

In later experiments the lead dioxide was mixed with an amount of sodium sulphate to provide the same volume fraction of the final cathode as was taken up by 2 wt.% graphite. All of the sodium sulphate crystals were smaller than 250  $\mu\text{m}$ ; 60% by weight were less than 100  $\mu\text{m}$ .

Cells were cycled at constant current. The end of discharge was judged by cell voltage, and cells were recharged for a period of time based on the length of the previous discharge.

Specimen sections of electrodes were prepared for post mortem SEM examination by drying, impregnating with an Araldite hot setting liquid (MY 750), and polymerising (DY 062) *in situ*.

Zeta potential measurements of the component solids from the cathodes (*i.e.*, graphite,  $\text{PbO}_2$  and  $\text{PbSO}_4$ ) were obtained by immobilising each, separately, on a microporous membrane in the apparatus shown in Fig. 1. The central tube terminates in a platinum mesh working electrode. Microporous membranes with mean pore sizes in the range 0.1 - 8  $\mu\text{m}$  were positioned in front of this electrode. The materials of interest were de-

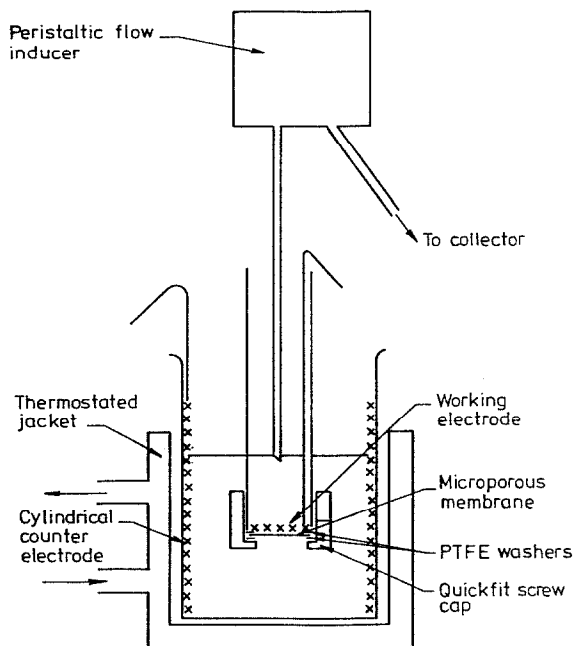


Fig. 1. The dipped cell apparatus.

posited to form a complete, uniform layer on the membrane, and a constant voltage was applied between the working electrode and a cylindrical platinum counter electrode placed around the inner surface of the vessel containing the apparatus. Extracts were removed from the dipped cell by a peristaltic flow inducer in such a way as to maintain the two parts of the cell in hydrostatic equilibrium. The rate of liquid transfer then provided a direct measurement of the zeta potential of the phase trapped on the porous membrane by application of the Smoluchowski equation:

$$\text{Volume flow rate } V = \frac{Ie\zeta}{4\pi\eta k_o}$$

where  $I$  is the current,  $\epsilon$  the dielectric constant,  $\zeta$  the zeta potential of the material,  $\eta$  the viscosity of the solvent and  $k_o$  the specific conductivity of the electrolyte.

## Results

The use of chemically prepared  $\text{PbO}_2$  in the preparation of flat plate positive electrodes is reported elsewhere [6 - 8]. It was necessary in those cases to incorporate an extra component in the active mass mix to perform a binder function until, after a few cycles, the plate had developed its own microstructure. In one case tetrabasic lead sulphate was mixed with the

$\text{PbO}_2$  [7] and the initial discharge capacity of the resultant plates was only 35% of the conventional equivalent. In another approach [6] a small quantity of polytetrafluoroethylene was incorporated, though this gave rise to some increase in resistance. For the present programme, positive plates of tubular design were used so that no binder material was necessary. They were constructed around a set of six, lead alloy spines projecting down from an alloy top plate. The active material was then packed in the annular space between each spine and a porous tubular sleeve. The bottom of each tube was plugged by a plastic cap.

#### *Discharge capacity experiments*

Cells containing  $\text{PbO}_2$  alone yielded little or no capacity, possibly due to poor electrolyte penetration. It was also found that  $\text{PbO}_2$  leached out through the tube. The addition of 10 wt.% graphite (~30 vol.%) appeared to improve electrolyte penetration, and when microporous liners were fitted inside the tubes (Fig. 2) a substantial initial discharge utilization was obtained which approached that of the commercial plate. However, when these two plates were cycled through a recharge/discharge sequence their capacities fell abruptly and then recovered gradually, as shown.

The origins of the difference between tubular plates with, and without, graphite were sought in an SEM study of sections through the plates.

Figure 3 shows that, overall, the cathode space containing 10 wt.% graphite was packed uniformly but, as shown in Fig. 4, the particles of  $\text{PbO}_2$  were separated.

After the electrode containing graphite had been partially discharged once (Fig. 5) an element of coarse voidage appeared and the regions which still contained solids were much more tightly packed than previously.

After the cell had been cycled 4 times the voidage volumes of the electrode had become substantial, but the active material (Fig. 6) was showing signs of developing a coralloid structure [10]. The microstructural

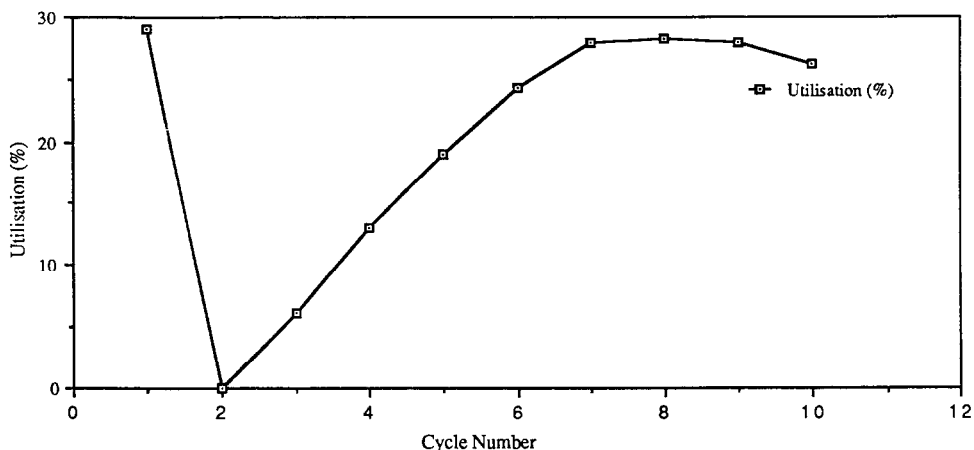


Fig. 2. Discharge capacities at cycles 1 - 10 of a plate containing 10 wt.% graphite.

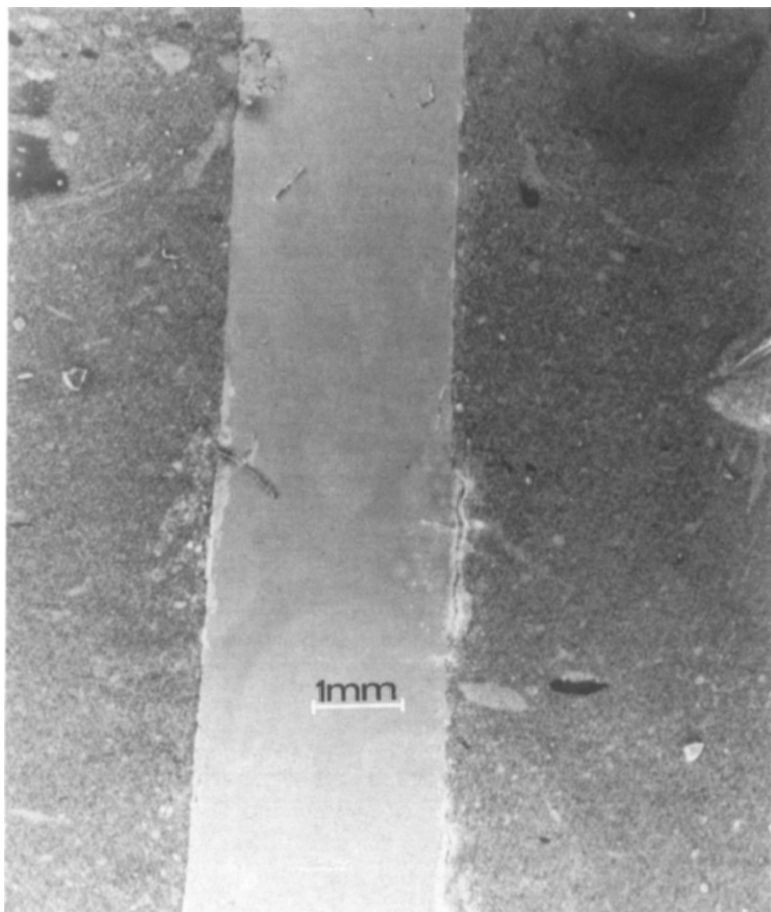


Fig. 3. Scanning electron micrograph of a positive plate containing 10 wt.% graphite before initial discharge.

changes which take place during early cycling of these plates, even to low depths of discharge, are quite dramatic, but it is significant that the progressive changes are towards a form which would be indistinguishable from that of a flat plate manufactured by conventional electrochemical forming procedures.

The initial series of experiments indicated that it was advantageous to have graphite intermixed with  $\text{PbO}_2$  for preparing tubular positive plates. It was not clear whether this advantage resulted from improvements in electrical conductivity in the plate, from assisted packing density, or from enhanced migration of the electrolyte.

Experiments in pursuit of the origin of the benefits of introducing graphite began with a systematic variation in the amount of additive. Details of composition and discharge capabilities are given in Table 1.

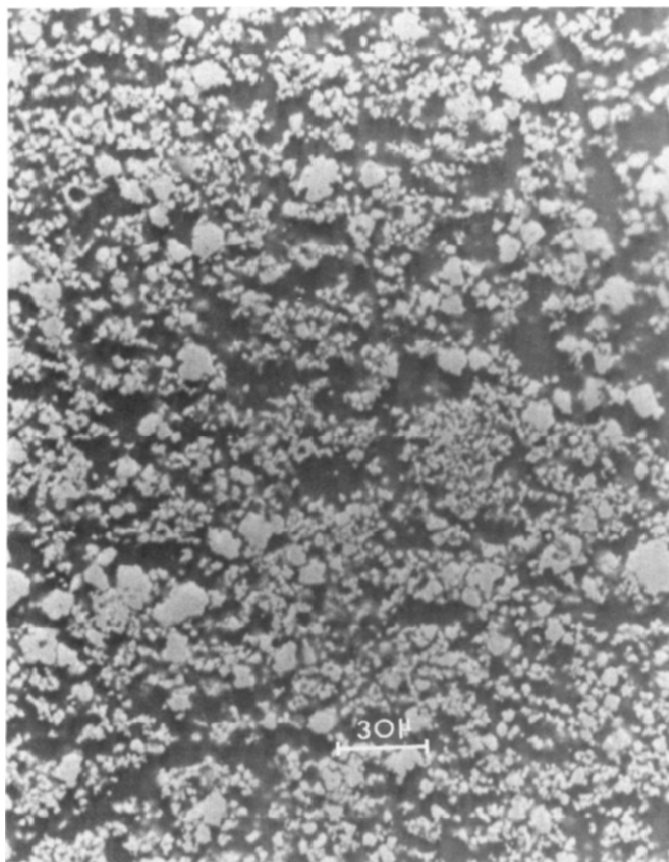


Fig. 4. Scanning electron micrograph of the active material in a plate containing 10 wt.% graphite before discharge. Higher magnification showing spacing between  $\text{PbO}_2$  particles.

The use of 12 wt.% graphite resulted in a low initial utilization of active material with a sharp fall at cycle 2. This was probably due to the development of voidage within the plate. When 5 wt.% graphite was used a much higher initial utilization was obtained, though this too fell at cycle 2. After remaining low at cycle 3, it then slowly recovered to its original level. The highest utilization of active materials was obtained at rather low concentrations of graphite, and this was sustained through the first few cycles with no significant fall-off.

In order to test whether the graphite was acting merely as a pore-forming agent, a separate experiment was devised in which  $\text{PbO}_2$  was mixed with  $\text{Na}_2\text{SO}_4$  to prepare electrodes. On immersion of the plate in the electrolyte the sodium sulphate dissolved and provided a known fraction of porosity. This experiment was carried out with two concentrations of  $\text{Na}_2\text{SO}_4$  and gave the results shown in Table 2.

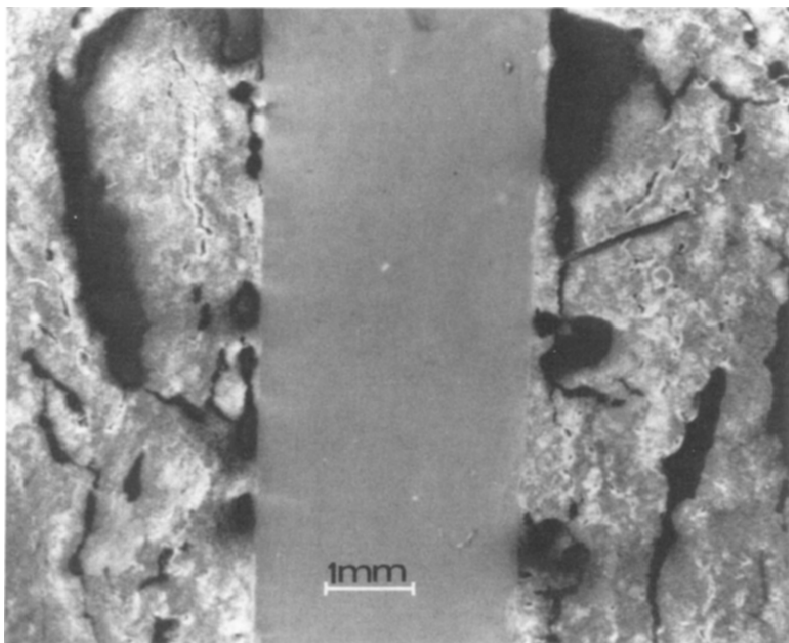


Fig. 5. Scanning electron micrograph of a positive plate containing 10 wt.% graphite after partial discharge.

#### *The role of the graphite*

It is clear from these results that porosity is advantageous in achieving high utilizations and, since the best results in the  $\text{PbO}_2\text{-C}$  series were obtained with the lowest graphite levels, the function of graphite may not have been predominantly as a pore-former. The same argument applies to any contribution graphite might make in improving electrical connections. Rather, it appears that the graphite assists with the irrigation of the porous electrode by the electrolyte. Two separate functions are important. Initially, the active material of the electrode prepared by chemical means is dry, and it is likely that the graphite assists the penetration of the electrode by the sulphuric acid by offering improved wetting characteristics. This was demonstrated by a simple bench test when lead dioxide powder and graphite were distributed separately on the surface of 5 M sulphuric acid contained in a beaker. Despite the difference in density of the two materials, the graphite sank to the bottom of the beaker while the  $\text{PbO}_2$  remained on the surface. This was an indication that the graphite was wetted by the acid while the  $\text{PbO}_2$  was not.

A second mode in which the graphite might assist the function of the tubular electrode involves the all-important transport of acid through the porous structure in support of the cell reaction [11]. Normally, the replenishment of sulphuric acid consumed in the plate pores by the electrode reaction is mainly by diffusive transport from the bulk electrolyte. However, except at very low discharge rates, this is unable to provide a sufficient flux to sustain the discharge. It is for this reason that active mass utilization



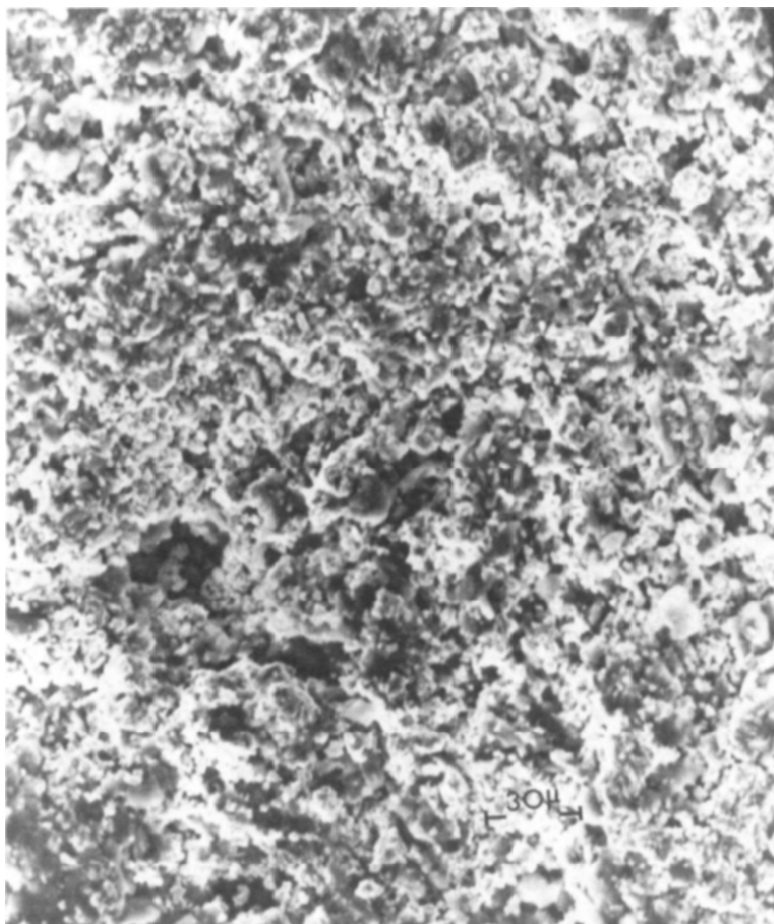


Fig. 6. Scanning electron micrograph of the active material in a plate containing 10 wt.% graphite after 4 discharge/charge cycles showing incipient development of a coralloid structure.

declines dramatically with increasing rate of discharge. However, in common with other solids, the component phases of the electrode will tend to acquire a surface electric charge when brought into contact with a polar liquid (the electrolyte). Each of the constituents of the active mass will have associated with it a characteristic zeta potential, and the possibility arises that the addition of a material with a high zeta potential of the correct polarity might allow the electro-osmotic pumping of the sulphuric acid through the structure. The flow rate due to electro-osmosis is given by the Smoluchowski equation (*vide supra*).

The importance of such an effect would be that the rate of pumping,  $V$ , would be inversely proportional to electrolyte concentration, so that as sulphuric acid was consumed within the electrode then the electro-osmosis

TABLE 1

Effect of graphite concentration on plate performance

| Graphite concentration (wt.%) | Packing densities (% of theoretical) | Theoretical discharge capacity (%) obtained at cycle |    |     |    |    |     |
|-------------------------------|--------------------------------------|--|----|-----|----|----|-----|
|                               |                                      | 1  | 2  | 3   | 4  | 5  | 6   |
| 12                            | 32                                   | 5  | 0  | 0.5 | 1  | 1  | 1.5 |
| 5                             | 36                                   | 22   | 4  | 3   | 15 | 17 | 20  |
| 1                             | 30                                   | 33   | 32 | 38  | 29 | 25 | 25  |
| 0                             | 37                                   | 1  |    |     |    |    |     |

TABLE 2

Effect of introducing porosity by mixing  $\text{Na}_2\text{SO}_4$  with  $\text{PbO}_2$  for tubular plate construction

| $\text{Na}_2\text{SO}_4$ concentration (wt.%) | Total packing efficiency ( $\text{PbO}_2 + \text{Na}_2\text{SO}_4$ ) | Theoretical capacity (%) obtained at cycle |     |      |      |
|---|--|--|-----|------|------|
|   |  | 1  | 2   | 3    | 4    |
| 3.8   | 39   | 15.1                                       | 5.6 | 10.4 | 12.7 |
| 2.2   | 36   | 2.4  | 2.8 | 2.8  | 2.4  |

would tend to increase — thus replenishing the plate with fresh electrolyte. The flow rate is also directly proportional to current density and so, for both these reasons, the effect would be expected to operate to match the demand put upon it by cell discharge.

In order to explore this possible function of the graphite in tubular plates, the zeta potentials of all the solid phases present were measured, and a test cell was constructed to see if the electro-osmotic pumping effect could be detected.

#### *Measurement of zeta potentials*

The zeta potentials of the several solid phases present in the acid-treated tubular plates were measured separately, as described in the Experimental Section. The results of measurements made at around pH 4 are summarized in Table 3.

It is not possible to measure zeta potentials with the dipped cell in full battery strength acid due to the low flow rates resulting from the significantly higher conductivity. In future, it will be important to know the magnitude of the zeta potential under these acidic conditions as well, in order to assess

TABLE 3  
Measured zeta potentials

| Material          | Treatment          | pH  | Zeta potential (mV) |
|-------------------|--------------------|-----|---------------------|
| Graphite          | As-received        | 4.2 | -21                 |
| Graphite          | 5 M sulphuric acid | 3.5 | -63                 |
| PbO <sub>2</sub>  | As-received        | 4.0 | 0                   |
| PbSO <sub>4</sub> | As-received        | 3.5 | -2                  |

the contribution to electrolyte transport from electro-osmotic pumping at the beginning of discharge. Materials with strongly acidic surface groups will remain fully ionized in 5 M H<sub>2</sub>SO<sub>4</sub>, thus presenting a negatively charged surface with a correspondingly high zeta potential. Less acidic groups may only be partially dissociated at these high acid strengths, and therefore display apparently lower zeta potentials and thus a reduced electro-osmotic pumping rate.

It is clear from these results that the only phase present in the tubular electrodes having a substantial zeta potential after contact with sulphuric acid is the graphite. This could be associated with the intercalation of HSO<sub>4</sub><sup>-</sup>, SO<sub>4</sub><sup>=</sup> into the lamellar graphite structure [12]. The HSO<sub>4</sub><sup>-</sup> group would remain ionised in 5 M H<sub>2</sub>SO<sub>4</sub>, providing a negative excess charge on the graphite surface where the edges of the layers were exposed to the solution.

In order to test the possibility that the zeta potential of the graphite will cause electro-osmotic pumping of the electrolyte into the microstructure of the cell during discharge, a special tubular cell with a perforated, tubular central spine was constructed (Fig. 7). The annular space of the tubular plate was packed with chemical PbO<sub>2</sub> and 2 wt.% graphite, and a tube was connected to the top of the tubular current collector. The electrode was set to soak in battery strength acid for 2 h and then the cell was allowed to discharge at 0.5 A for 0.5 h. During this time 6 ml of electrolyte were expelled from the tube. This is close to what would be predicted on the basis of electro-osmotic pumping.

These experiments indicate that graphite assists the function of the positive plate, both by improving the wetting of the electrode when it is initially immersed in the electrolyte, and also during service, by assisting with the supply of sulphuric acid in support of the cell reaction. There is no reason why this latter function should be confined to tubular plates made from chemically prepared PbO<sub>2</sub>, and it will be important to examine the consequences when materials, such as graphite, with high zeta potentials are admixed during the preparation of conventional plates.

A significant enhancement has been reported in the performance of flat plate cells made by conventional methods as a result of the addition of graphite to the paste prior to formation [9]. However, the authors have,

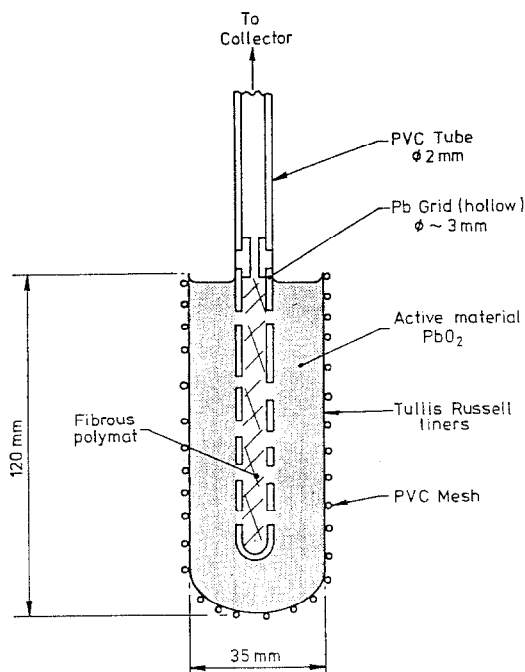


Fig. 7. Tubular cell with hollow central current collector allowing expulsion of electrolyte pumped by electro-osmosis.

in our opinion, mistakenly attributed these improvements simply to changes in the plate porosity, which on its own cannot explain the dramatically improved uniformity of discharge product distribution through the thickness of the plate. Electro-osmosis though, due to its more effective replenishment of electrolyte within the plate pores, is more likely to have been responsible. As the graphite was slowly consumed by oxidation under the anodic overcharge conditions, it will be important to investigate alternative materials which have a greater resistance to degradation, while still maintaining high zeta potentials.

In the ideal situation, the electro-osmotic pumping should be able, at least, to match the demand for electrolyte by the electrode discharge reaction in order to maintain local acidity and, hence, prevent polarization.

In the absence of convective transport, the flux of acid required for the positive plate discharge is modified by ionic migration [11]

$$\frac{-I}{n|F} = \frac{D\nabla C}{(3 - 2t_+)}$$

where  $D\nabla C$  is the diffusive transport;  $t_+$ , the transport number for  $H^+$ , is  $\sim 0.8$  in 5 M  $H_2SO_4$ , and  $n = 2$ , as



$-I(3 - 2t_+)/|n|F$  therefore represents the flux of acid required in moles  $s^{-1} cm^{-2}$ , where  $I$  is  $A cm^{-2}$ . This can be related to a volume flow rate, as full strength battery acid is 5.5 M in  $H_2SO_4$ :

$$\frac{-I \times 1.4 \times 1000}{2 \times 96487 \times 5.5} \text{ ml s}^{-1} \text{ cm}^{-2}$$

This, in turn, can be equated to the electro-osmotic flow [13]

$$V = \frac{8 \times 10^{-6} I \zeta}{k_o} \text{ cm}^3 \text{ s}^{-1}$$

where  $\zeta$  is the zeta potential (mV),  $I$  is the current ( $A cm^{-2}$ ) and  $k_o$  is the specific conductivity ( $\Omega cm$ ) $^{-1}$ .

On rearranging,

$$\zeta = \frac{-1.32 \times 10^{-3}}{8 \times 10^{-6}} k_o$$

For full strength battery acid,  $k_o \sim 0.66 (\Omega cm)^{-1}$ , requiring  $\zeta$  to be  $-110$  mV. For depleted acid in the pores of the plate,  $k_o$  will be lower — thus reducing the magnitude needed for  $\zeta$ , though it should also be remembered that the fraction of current still flowing in the electrolyte phase, rather than in the  $PbO_2$ , will also have been reduced.

For electro-osmotic effects in the positive plate on discharge, a high negative zeta potential is needed (Fig. 8). In these highly acidic solutions, this can only be provided by a strong acid species — such as  $HSO_4^-$  — immobilized on the ends of the graphite layer structure. More oxidation-resistant substrates to adsorb  $HSO_4^-$  may be available, thus making this more suitable for battery use. Alternative materials, such as polymers with pendant benzene sulphonate groups, would only have a  $pK$  of  $\sim 0.7$  — which would essentially be undissociated in 5.5 M  $H_2SO_4$ . However, the

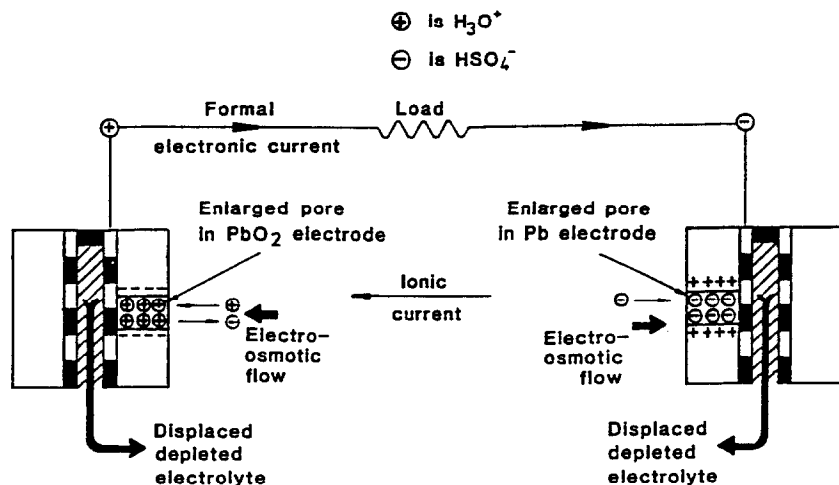
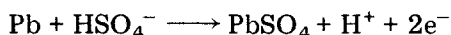


Fig. 8. Current and electro-osmotic flows during cell discharge.

acidity of this group may be increased further by substituting the benzene ring with Cl and NO<sub>2</sub>. The resulting material should be less easily oxidized than graphite under acid conditions. The effectiveness of this electro-osmotic flow enhancement may be greatly helped by designing the electrode so that the depleted electrolyte may leave in such a way as not to impede the influx of fresh acid (*e.g.*, by having a central portion of a sandwich grid structure filled with fibrous propylene as a route back to the bulk electrolyte — Fig. 8). This could also cause electrolyte mixing, thus minimizing stratification.

For similar electro-osmotic effects in the negative plates:



requires a flux of acid equivalent to

$$\frac{I(2t_+ - 1)}{|n|F} \equiv \frac{I \times 0.6 \times 1000}{2 \times 96487 \times 5.5} \text{ ml s}^{-1} \text{ cm}^{-2}$$

Following the same form of calculation as above,  $\zeta = +47$  mV under strong acid conditions for the corresponding electro-osmotic flow inducing material incorporated in the negative plate structure (Fig. 8). The sign of the charge is opposite to that in the PbO<sub>2</sub> electrode in order that the sulphate flow should be into the electrode — in a direction opposed to the formal current. The flow-inducing material should not be reducible, nor soluble in sulphuric acid, *e.g.*, Cr<sub>2</sub>O<sub>3</sub>, and possibly other ceramic materials which, while thermodynamically soluble, may be kinetically stable, *e.g.*, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>. Alternatively, pyridinium or tertiary or quaternary ammonium groups immobilized on a polymeric framework, as in anionic exchange resins, should also be suitable.

For both electrodes, the particle size of the material introduced into the structure to encourage electro-osmotic flow should be significantly smaller than the active material aggregates — possibly only 1/10 — so that they become lodged in the pores through the electrode without blocking them. Typically, they may need to be in the range 0.5 - 5 μm.

The improved acid access to the internal surfaces of the plate can improve active material utilization, even at higher discharge rates, and also the uniformity of discharge through the plate thickness may have benefits in increasing the cycle life for a variety of reasons. These include a spread of the volume increase in active mass arising from the discharge reaction throughout the electrode — thus decreasing uneven mechanical stresses; cycling more of the active material, thus increasing the life of the cell by reducing the extremes of depth of discharge experienced by any part of the plate; maintaining electrolyte acidity at the grid/active mass interface, which may prevent PbO formation at the end of discharge from the grid material, and thus retard the progressive corrosion of the grid.

On recharge, a concentrated sulphuric acid solution is formed in the pores of the electrodes. This will diffuse into the bulk of the electrolyte, with some assistance from electro-osmosis, though due to the high local

conductivity this may not be as effective as on discharge. The higher density of this more concentrated acid causes it to sink down the face of the electrode to the bottom of the cell, building up a stronger acid solution there. This stratification of the electrolyte leads to problems of reduced utilization and plate life, especially in duty cycles where top of charge gassing is avoided — as only the active material in the lower part of the plate is subsequently fully cycled. The deeper local cycling experienced here ultimately leads to a premature loss of capacity. Bulk circulation of the electrolyte by an external pump has been demonstrated to circumvent this effect [14]. Not only does the capacity improve due to the reduced concentration polarization, but only 5% overcharge is needed to restore the cell to full capacity. This reduces gassing damage to the plate and improves the overall energy efficiency of the cell. However, instead of using an external pump to circulate the electrolyte (with the associated parasitic load on the battery that this involves), it may prove possible to utilize electro-osmosis as an *in situ* pump to mix the electrolyte on recharge, in addition to the circulation induced during discharge, as described above. This could be achieved by incorporating one or more layers in the separator with a high zeta potential, such that the electrolyte being transported through it by electro-osmosis in the more dilute, lower conductivity acid regions is being replaced by convection from the stronger acid at the bottom of the cell — thus effectively mixing the acid.

#### *Factors limiting the utilization of active material in positive plates*

The discharge capacities of the plates described above are profoundly influenced by microstructure. Plates that are packed tightly and do not contain graphite yield virtually no capacity, while plates that are loosely packed yield substantial utilization of active material initially, but undergo restructuring as they are cycled. After a few cycles the microstructure evolves into a form similar to that found in conventional-cycled flat plates. The dramatic loss of capacity in cycles 2 and 3 of plates with more than around 3 wt.% graphite is almost certainly due to a loss of structural integrity. Experiments in which the lead alloy spines were given a protective anodic treatment in lead acetate and sulphuric acid led to some improvements (*cf.* Figs. 9 and 10).

In the light of these results it does not appear that the use of chemically prepared  $\text{PbO}_2$  on its own will lead to a microstructure which will allow much greater utilization. Where gravimetric utilizations have been greater than those of commercial plates, due to greater porosity the volumetric utilization has been lower than that of the commercial equivalent. When used in combination with the protective anodic treatment and a suitable electro-osmotic pumping agent a consistently improved utilization may be achievable. An advantage may accrue, however, in the economy of the electrical forming process, which is very inefficient in the conversion of presently-used pastes.

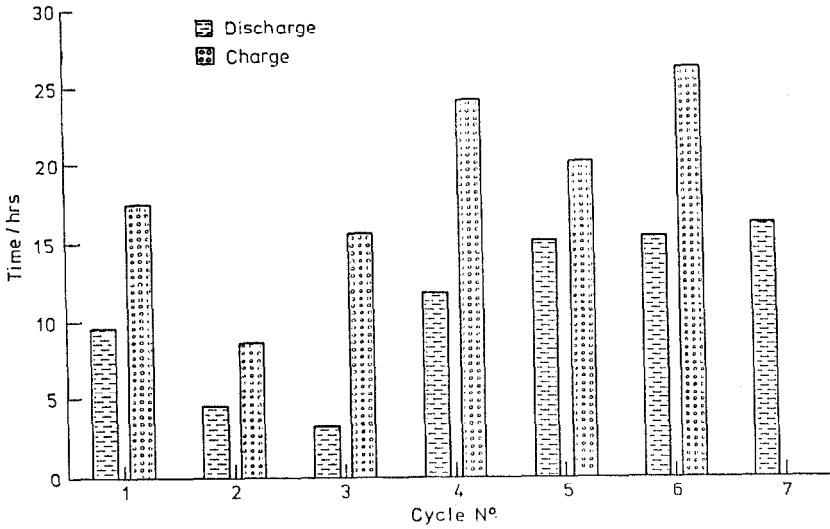


Fig. 9. Discharge and recharge capacity (at 1 A) of plate with no anodic treatment.

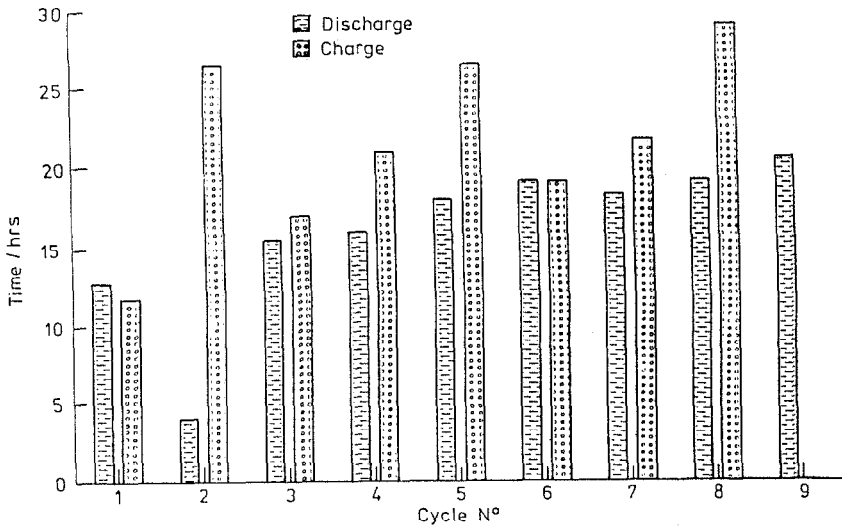


Fig. 10. Discharge and recharge capacity (at 1 A) of plate with anodic treatment in lead acetate and sulphuric acid.

## Conclusions

The ultimate capacity of a  $\text{PbO}_2$  plate is limited by a trade-off between transport processes, which improve with increased porosity, and by loss of structural coherence through the charge-discharge cycle which becomes



more severe with increased porosity. Although the limitations imposed by the microstructure dictate that, whichever route is used in preparation, the ultimate discharge capacity offered by plates of sensible thickness will be nowhere near 100%, there are good prospects that the use of additives in the positive active mass could promote good utilisations in cases where plates were designed for high cycle life.

The selection of materials and methods of deploying additives will not be straightforward, however, in view of the several different (and sometimes conflicting) ways in which the additives can influence the plate discharge process. Evidence presented here is consistent with a pore forming role and an electro-osmotic pumping function at least.

There is room for a great deal more work in the design and use of positive plate additives before a significant degree of optimisation can be confidently claimed.

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