LIMITATIONS IN THE DESIGN OF LEAD–ACID CELLS WITH IMMOBILIZED ELECTROLYTE

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Summary

The paper discusses the consequences of using a porous separator which completely occupies the interelectrode space and immobilizes the electrolyte. Transport equations which have been derived for the separator region, assuming planar electrodes, are presented with both rigorous and approximate solutions for long and short periods of time

The results are used to calculate the separator thickness necessary to avoid acid depletion at the positive plate surface. The dependence of this thickness on the rated capacity of the plate, the discharge time, and the separator properties expressed by the porosity and the tortuosity factor is then discussed. It is shown that for a given discharge rate there is an upper limit for the positive plate capacity, which is determined by the above mentioned separator properties.

Introduction

In the lead–acid battery the sulfuric acid serves as a component of the discharge reaction as well as the electrolyte As only part of the acid used during the discharge can be contained in the pores of the electrodes, the amount of acid in the interelectrode space and the transport of the acid to the electrode surface may be a critical factor limiting cell performance

In the normal (starting, lighting, ignition — SLI) battery a separator is usually placed in contact with the negative plate, and there is a free volume filled with acid between the separator and the positive plate This permits acid transport by convection to the positive plate where transport limitations are more critical For small, "non spillable" lead–acid batteries and for sealed cells it is customary to use a separator, which completely fills the space between the plates and immobilizes the acid in this region. Recently, the same design has been proposed for batteries intended for vehicle traction (EV) applications [1] The use of a porous separator in contact with both plates helps to prevent shedding of, and improve contact with, the active

material The elimination of convective transport, however, makes diffusion and migratory transport in the separator region critical

To estimate the importance of this limitation the transport phenomena in the separator region must be investigated and their effect on battery performance evaluated

Due to the coupling of transport in the separator with transport in the porous electrodes an exhaustive description of concentration profiles, etc , can only be accomplished by numerical methods involving transport and charge transfer in the porous electrodes The simulation of electrode performance has been treated by several authors [2] but only Tiedemann *et al* [3] has considered transport in the porous separator and, even in this case, it was assumed that there was a stirred reservoir of acid in contact with the positive plate Nevertheless, they found that the capacity of the battery configuration used for the simulations was limited by the amount of acid in the interelectrode space and the reservoir

In this paper the authors show how the immobilization of the electrolyte and the separator properties can influence the rate capability and energy density of the battery For this purpose, numerical methods, as used by the workers cited above, are less suited and an analytical treatment appears better, even if it involves some serious limitations in the underlying model Recently, a similar approach was chosen by Turner *et al* [4], but with a different objective. Their mathematical treatment was also too inaccurate in the time domain considered important for the present purpose

In the following simplified model the key points are that the capacity of the plate at the discharge rate in question is independent of transport in the separator region and that the major part of the acid in the plate pores is used up at the end of the discharge Thus, the purpose is to identify the conditions necessary to avoid depletion of the acid at the separator/plate interface before the plate has delivered its rated capacity

The physical model*

Consider two plane electrodes, Pb and PbO_2, separated by a porous separator of thickness d, saturated with sulfuric acid (Fig 1) The following
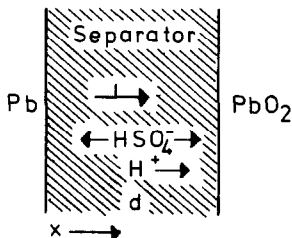

Fig 1 Model of separator region

*For list of symbols see end of paper

assumptions are part of the model The acid is a binary electrolyte complete-ly dissociated into H^+ and HSO_4^- [5] Zero electrolyte and electrode volume changes have been assumed although, in practice, it is the total volume which remains constant, with reductions in one being compensated by increases in the other (*loc cit* p 68). The acid is immobilized in the pores of the separa-tor thus eliminating transport by convection

Under these circumstances it is a reasonable approximation to use the one-dimensional Nernst–Planck equation

$$J_1 = -D_1 \left(\frac{dc_1}{dx} + \frac{z_1 F}{RT} c_1 \frac{d\phi}{dx} \right) \tag{1}$$

to describe the transport

The solution of the mass transport problem is then obtained by com-bination with the conservation equation

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x} \tag{2}$$

In order to obtain a simple analytical description, D_1 in eqn (1) is assumed to be independent of the concentration

Mathematical model

Electroneutrality requires that $c_+ = c_- = c$ Then, when $0 < x < d$, using eqns (1) and (2) for H^+ and HSO_4^- we get

$$\frac{\partial c}{\partial t} = D_+ \left(\frac{\partial^2 c}{\partial x^2} + \frac{F}{RT} \frac{\partial c}{\partial x} \frac{\partial \phi}{\partial x} \right)$$
$$\frac{\partial c}{\partial t} = D_- \left(\frac{\partial^2 c}{\partial x^2} - \frac{F}{RT} \frac{\partial c}{\partial x} \frac{\partial \phi}{\partial x} \right) \tag{3}$$

as $\partial^2 \phi / \partial x^2 = 0$ (no space charge in the region) Eliminating the terms contain-ing the electrical potential gives

$$\frac{\partial c}{\partial t} = \frac{2D_+ D_-}{D_+ + D_-} \frac{\partial^2 c}{\partial x^2} \equiv D \frac{\partial^2 c}{\partial x^2}, D = \frac{2D_+ D_-}{D_+ + D_-} \tag{4}$$

where D is the diffusion coefficient in the separator for H_2SO_4 as a neutral species

The solution of the partial second order differential equation, (4), requires one initial and two boundary conditions The initial condition is

$$t = 0, c = c^0 \tag{5}$$

where c^0 is the sulfuric acid concentration in the charged condition

The boundary conditions are given by the fluxes at $x = 0$ (Pb electrode) and $x = d$ (PbO_2 electrode) These are found as follows

Pb electrode $Pb + HSO_4^- \rightarrow PbSO_4 + H^+ + 2e$

$$J_+(x = 0) = \frac{\iota}{2F} = -D_+\left(\frac{dc}{dx} + \frac{F}{RT}c\frac{d\phi}{dx}\right)$$

$$J_-(x = 0) = \frac{-\iota}{2F} = -D_-\left(\frac{dc}{dx} - \frac{F}{RT}c\frac{d\phi}{dx}\right)$$

(6)

Eliminating $d\phi/dx$ and using $t_+ = D_+/(D_+ + D_-)$ gives

$$\frac{dc}{dx}\bigg|_{x=0} = \frac{\iota}{FD}(t_+ - \tfrac{1}{2})$$

(7)

PbO_2 electrode $PbO_2 + 3H^+ + HSO_4^- + 2e \rightarrow PbSO_4 + 2H_2O$

$$J_+(x = d) = \frac{3\iota}{2F} = -D_+\left(\frac{dc}{dx} + \frac{F}{RT}c\frac{d\phi}{dx}\right)$$

$$J_-(x = d) = \frac{\iota}{2F} = -D_-\left(\frac{dc}{dx} - \frac{F}{RT}c\frac{d\phi}{dx}\right)$$

(8)

which gives

$$\frac{dc}{dx}\bigg|_{x=d} = \frac{\iota}{FD}(t_+ - 3/2)$$

(9)

For constant current discharges, the boundary conditions are time independent and a simple solution of eqns. (4), (5), (7), and (9) is possible For heat conduction problems Carslaw and Jaeger [6] have derived solutions of the system $\partial U/\partial t = D\ \partial^2 U/\partial x^2$ with the initial condition $U = 0$ and the boundary conditions $dU/dx|_{x=0} = 0$ and $dU/dx|_{x=d} = \alpha$

Using $c - c^0$ as independent variable and combining solutions for x and $d - x$ as spatial variables [7], one arrives at the following equivalent rigorous solutions

$$c = c^0 + (\alpha_2 - \alpha_1)tD/d + (\alpha_2 - \alpha_1)x^2/2d + \alpha_1 x - (2\alpha_1 + \alpha_2)d/6$$

(10)

$$-2d/\pi^2 \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp[-n^2\pi^2 T](\alpha_2\cos[n\pi x/d] - \alpha_1\cos[n\pi(d-x)/d])$$

(11)

and the "erf" type of solution (for ierfc see ref 8)

$$c = c^{0\cdot} + 2\sqrt{tD} \sum_{n=0}^{\infty} \alpha_2[\text{ierfc}[(2n + 1 + x/d)/2\sqrt{T}]$$

$$+ \text{ierfc}[(2n + 1 - x/d)/2\sqrt{T}]] - \alpha_1[\text{ierfc}[(2n + x/d)/2\sqrt{T}]$$

$$+ \text{ierfc}[(2n - x/d)/2\sqrt{T}]]$$

(12)

where $\alpha_1 = (t_+ - \frac{1}{2})i/FD$ and $\alpha_2 = (t_+ - 3/2)i/FD$ and T is a dimensionless time ratio, $T = t/\tau$ τ is the time constant for diffusion in the separator layer $\tau = d^2/D$. The magnitude of τ delineates the time regions where eqns (11) and (12) degenerate into simpler approximate solutions For "small T", eqn (12) can be simplified to

$$c = c^0 \; - \; \frac{2i}{F}(t/D)^{1/2} \; (3/2 - t_+) \; \text{ierfc} \; \frac{1 - x/d}{2\sqrt{T}} + (t_+ - \tfrac{1}{2}) \left[\text{ierfc} \; \frac{x/d}{2\sqrt{T}} \right] \qquad (13)$$

where the value of the α's has been introduced
    For "large T", eqn. (11) gives

$$c = c^0 \; - \; \frac{it}{Fd} \; - \; \frac{i}{FD} \left[\frac{x^2}{2d} \; - \; (t_+ - \tfrac{1}{2})x + (\tfrac{1}{2}t_+ - 5/12)d] \right] \qquad (14)$$

as the exponentials vanish.
    Equations (13) and (14) are limiting solutions for $T \to 0$ and $T \to \infty$, respectively They are, however, very good approximations over a broad range of time regions For the positive plate ($x = d$) the rigorous solution, eqn (11), and the approximate solutions, eqns (13) and (14), can be written as

$$\frac{Fd(c^0 - c)}{i\tau} = \begin{cases} T - \tfrac{1}{2}t_+ + 7/12 - \displaystyle\sum_1^\infty \frac{1}{n^2\pi^2}[3/2 - t_+ + (-1)^n(t_+ - \tfrac{1}{2})] \\[4pt] \quad \exp(-n^2\pi^2T) & (15a) \\[12pt] 2(3/2 - t_+)(T/\pi)^{1/2} & (15b) \\[12pt] T - \tfrac{1}{2}t_+ + 7/12 & (15c) \end{cases}$$

    On Fig. 2, $Fd(c^0 - c)/(i\tau)$, calculated for $t_+ = 0.8$, is shown as a function of T according to the three expressions It can be seen that for $T < 0.15$ and for $T > 0.21$ eqns (15b) and (15c), respectively, are very good approximations to eqn (15a) Even in the middle of the transition region at $T = 0.18$ the deviation of either approximation from the exact value is less than 5% Thus the square root approximation, eqn. (15b), will be used for $t < 0.18\,\tau$ and the linear approximation, eqn. (15c), for $t > 0.18\,\tau$.
    It can be seen that the development of the sulfuric acid concentration profile in the separator region starts with ierfc profiles at each electrode

At the negative plate

$$c = c^0 \; - \; \frac{2i}{F} \; (t/D)^{1/2}(t_+ - \tfrac{1}{2}) \; \text{ierfc} \; \frac{x/d}{2\sqrt{T}} \qquad (16a)$$
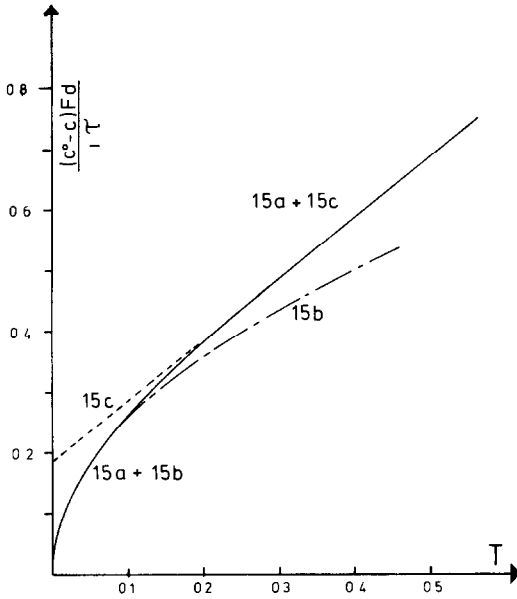
Fig 2 Dimensionless concentration as function of dimensionless time, T Equation (15a, b, c) compared

and the positive plate

$$c = c^0 - \frac{2\iota}{F}(t/D)^{1/2}(3/2 - t_+)\,\text{ierfc}\,\frac{1 - x/d}{2\sqrt{T}} \tag{16b}$$

for $t < 0\,18\,\tau$

These profiles meet and transform, for $t > 0.18\,\tau$, into a parabola given by eqn (14) with a vertex at $x = (t_+ - \frac{1}{2})d \simeq 0\,3d$ At this point $dc/dx = 0$ for all t and there is no net transport of acid across the plane parallel to the electrode through the vertex

This point then divides the separator region into an anodic and a cathodic part The development of the concentration profiles is illustrated in Fig 3 The acid concentrations at the negative and positive plate surfaces, c_n and c_p are given by

For $t < 0\,18\,\tau$

$$c_n = c^0 - \frac{2\iota}{F}(t/\pi D)^{1/2}(t_+ - \frac{1}{2}) \tag{17a}$$

$$c_p = c^0 - \frac{2\iota}{F}(t/\pi D)^{1/2}(3/2 - t_+) \tag{17b}$$

as ierfc$(0) = 1/\sqrt{\pi}$

and for $t > 0\,18\,\tau$

$$c_n = c^0 - \frac{\iota}{F}\left(\frac{t}{d} + \frac{d}{D}(\tfrac{1}{2}t_+ - 5/12)\right) \tag{18a}$$
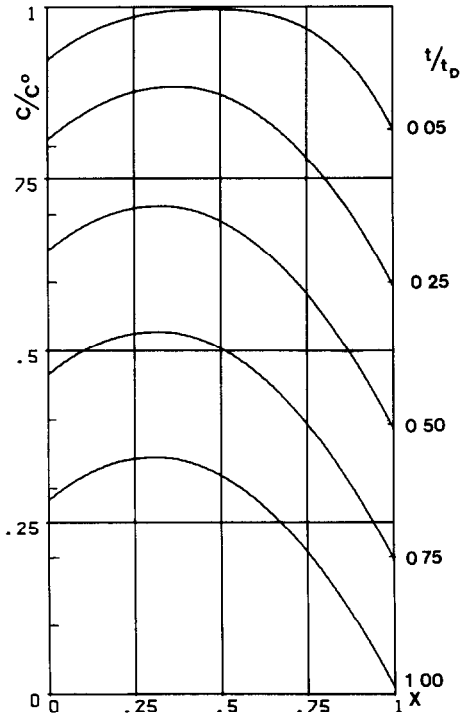
Fig 3 Concentration profiles in the separator region during discharge $Q = 100$ C cm^{-2}, $d = 0.4$ cm, $t_D = 3$ h, $c^0 = 3.5$ mol dm^{-3}, $D = 0.8 \times 10^{-5}$ cm^2 s^{-1}, t/t_D as indicated

$$c_p = c^0 - \frac{\iota}{F}\left(\frac{t}{d} + \frac{d}{D}(7/12 - \tfrac{1}{2}t_+)\right) \tag{18b}$$

Equations (17) and (18) enable the changes in acid concentration at the electrode surfaces during discharge to be calculated, provided that the acid contained in the pores of the electrodes can be neglected This is, of course, not acceptable and, in the following, corrections are introduced to compensate for this

The effect of transport in the separator region

As t_+ is about 0.8 [9], it can be seen from eqns (17) and (18) and also from Fig 3, that the concentration at the positive plate, c_p, is critical If this concentration drops below a minimum value, c_{min}, further transport of the remaining acid from the separator into the plate is impeded, and the battery voltage drops off sharply If the transport is too slow, or the amount of acid insufficient, this may happen before the plate has fully discharged and the battery capacity is then limited by the transport in the separator layer.

The decline of c_p during discharge is controlled by the discharge rate and three parameters characteristic for the separator region the initial concentration, c^0, the effective diffusion coefficient, D, and the thickness, d

In the expressions developed above the actual values of the parameters D and c^0, as well as the definition of the variables c and x, depend on the porosity and tortuosity of the separator. The concentrations c, c^0, c_n and c_p are measured relative to unit separator volume, and D is an effective diffusion coefficient for diffusion through the separator relative to a coordinate axis perpendicular to the electrode surface. The implications of this are discussed in more detail in Appendix A

In the following, a commercial separator material with low porosity (0 65) and high tortuosity (1.3) is used to illustrate the principles of the computations Using this separator, c^0 is reduced from 5 mol dm^{-3} in the free acid to 3.3 mol dm^{-3} in the separator and D is reduced by a factor 2

Based on data from ref. 10 Micka and Rousar [11] have expressed the diffusion coefficient for H_2SO_4 in water as

$$D_1/\text{cm}^2\,\text{s}^{-1} = 10^{-5}(1.48 + 0\ 125\ c^0/\text{mol dm}^{-3}) \qquad (19)$$

To be on the safe side the value for D_1 for 1 mol dm^{-3} was used for the following calculations and gives an effective diffusion coefficient, D, in the commercial separator of 0.8×10^{-5} cm^2 s^{-1}

The optimum thickness of the separator layer

The more hindered is the transport, the steeper are the slopes of the concentration profiles. Thus it can be seen from Fig. 3 that the average acid concentration at the end of discharge will be higher when a separator which hinders the transport is present, $\imath e$, more acid must be used to obtain a given capacity.

The spacing, d, depends primarily on the rated capacity per unit area of the positive plate, Q, but also, for the reason mentioned above, on the discharge rate and on the properties of the separator. Q should be determined under conditions where acid depletion takes place simultaneously in the pores and in the free electrolyte between the plates The magnitude of Q depends primarily on the thickness of the positive plate and on the discharge rate. Q is usually in the range of 60 - 250 C cm^{-2} corresponding to a capacity of 6 - 25 A h for a 180 cm^2 plate (two sides)

At constant current the discharge rate is most conveniently expressed as the time, t_D, needed for complete discharge of the battery. A typical application for advanced lead–acid batteries is the propulsion of electrical vehicles. To simulate this use a 3 h discharge has been proposed [12], but the behaviour at higher and lower rates may also be important.

A minimum value for d results from the need for maintaining equilibrium in the separator layer, $\imath e$, under conditions where the transport rate in the separator is fast compared with the discharge time. Then the total amount of acid necessary for full utilization of the plate capacity is Q/F mol cm^{-2}. A certain fraction, r, is already present in the plate pores, however, and thus

$$d_{min} = (1 - r)Q/(F(c^0 - c_{min})) \tag{20}$$

where c_{min} is the lowest acceptable acid concentration at the end of discharge The magnitude of r is discussed in Appendix B

For $Q = 125$ C cm^{-2}, $c^0 - c_{min} = 3$ mol dm^{-3} and $r = 0$ 3, d_{min} is 3 mm The time constant $\tau = d^2/D$ is then 3 1 h and consequently, in this case, eqn. (20) is a good estimate for $t_D = 20$ h or larger. At faster discharge rates, however, a part of the acid in the separator region is not utilized, and for $d = d_{min}$, c_p will approach c_{min} before the positive plate has delivered its rated capacity Let the time when this happens be t^*, then t^* can be found from eqns (11) or (12) inserting $x = d$, and $t = t^*$. Introducing $\iota = Q/t_D$ and using $t_+ = 0$ 8, eqn (11) takes the form

$$c^0 - c_{min} = \frac{Q}{Fd}\frac{t^*}{t_D} + \frac{Qd}{FDt_D}\left(0\ 18 - 2\sum_{n=1}^{\infty}\frac{1}{n^2\pi^2}\right.$$

$$\left. \times\ (0\ 7 + (-1)^n 0\ 3)\exp[-n^2\pi^2 t^*/\tau]\right) \tag{21}$$

Using $c^0 - c_{min} = 3$ mol dm^{-3} and $D = 0$ 8 $\times 10^{-5}$ cm^2 s^{-1}, and inserting selected values for Q and t_D, t^* is found as a function of d and compared with t_D

In Fig 4 t^*/t_D is plotted as a function of d for $Q = 125$ C cm^{-2} and for $t_D = 3$ h At small values of d, t^* increases linearly with d, but when $d > 3$ mm t^*/t_D levels off and asymptotically approaches a value of about 0.8 Thus, in this case apparently, the positive plate can never be discharged completely, even with a large surplus of acid (large d) due to the restrictions on the transport in the separator

These calculations, however, do not include the effect of the acid contained in the plate pores. It can be assumed that this acid is used before t^* is reached. Thus, the rated capacity can be obtained for $t^*/t_D > 1 - r$, which is estimated to be 0 75 From Fig 4 it can be seen that this condition is obtained for $d \geqslant 8$ mm This is, however, an unacceptably large separator thickness, both from an energy and from a power density point of view To obtain a reasonable battery design using this separator, the specific plate capacity must be reduced.

To illustrate these relations t^*/t_D is shown, as function of d in Fig 5 for $t_D = 3$ h and for different values of Q Corresponding curves are shown in Fig 6 for $Q = 110$ C cm^{-2} and for different values of t_D It is seen that the limiting phenomena discussed above take place for large values of Q and small values of t_D They are obviously caused by the semi-infinite diffusion mode which occurs for large values of d For example, for $d = 8$ mm the time constant is 22 h, and consequently for $t_D = 3$ h the correct approximation to use is eqn (17b) Inserting $t^*/t_D \geqslant 1 - r$ and $\iota = Q/t_D$ gives the following limit for Q

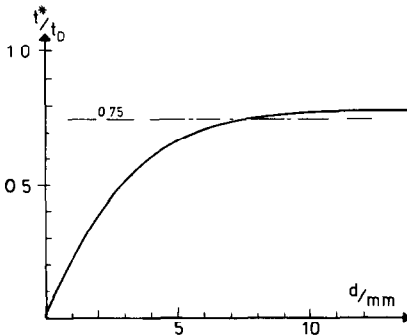$$Q < Q_{max} = \frac{F\sqrt{\pi}}{3 - 2t_+}(c^0 - c_{min})\left(\frac{t_D D}{(1 - r)}\right)^{1/2} \tag{22}$$

Fig 4 t^*/t_D as function of d $c^0 - c_{mm} = 3$ mol dm^{-3}, $D = 0\,8 \times 10^{-5}$ cm^2 s^{-1}, $Q = 125$ C cm^{-2}
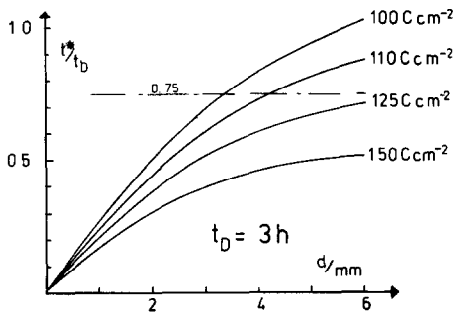

Fig 5 t^*/t_D as function of d for different values of Q as indicated $t_D = 3$ h, separator values as in Fig 4
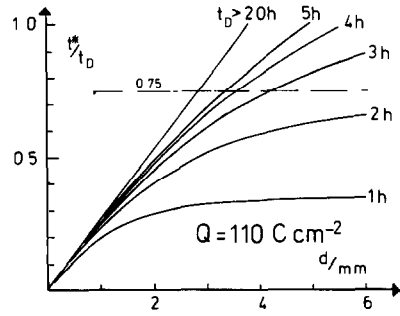
Fig 6 t^*/t_D for different values of t_D as indicated $Q = 110$ C cm^{-2}, separator values as in Fig 4

For the data used in Fig. 4, Q_{max} is found to be 125.1 C cm^{-2} Conversely, for a given Q, the minimum value for the discharge time can be found from eqn (22).

A simple, explicit solution for d for a given Q and t_D cannot be found from eqn (21). For high energy density batteries, however, it is an obvious requirement that the utilization of the acid should be more than 50%, i e , $d < 2d_{min}$ It can be shown that under this restriction the linear approximation, eqn. (18b), holds Inserting $t/t_D = 1 - r$ and $i = Q/t_D$ gives rise to a quadratic equation in d.

$$\frac{(7/12 - t_+/2)Q}{FDt_D} \times d^2 - (c^0 - c_{min}) \times d + (1 - r)\frac{Q}{F} = 0 \qquad (23)$$

with the solution

$$d = \frac{(c^0 - c_{min})FDt_D}{2(7/12 - t_+/2)Q} \left[1 - \left(1 - \frac{4(1 - r)(7/12 - t_+/2)Q^2}{F^2(c^0 - c_{min})^2 Dt_D}\right)^{1/2}\right] \qquad (24)$$

d_{min}/d is an indication of the utilization of the acid in the separator region The reciprocal of this ratio can be expressed rather simply by the ratio Q/Q_{max} Inserting eqns. (20) and (21) into eqn. (24) gives

$$\frac{d}{d_{min}} = \frac{(3-2t_+)^2}{2\pi(7/12 - t_+/2)} \left(\frac{Q_{max}}{Q}\right)^2 \left[1 - \left(1 - \frac{4\pi(7/12 - t_+/2)}{(3-2t_+)^2}\left(\frac{Q}{Q_{max}}\right)^2\right)^{1/2}\right]$$

(25a)

Inserting $t_+ = 0.8$, eqn (25a) becomes

$$\frac{d}{d_{min}} = 1\ 702\left(\frac{Q_{max}}{Q}\right)^2\left[1 - \left(1 - 1\ 175\left(\frac{Q}{Q_{max}}\right)^2\right)^{1/2}\right]$$

(25b)

Equation (25a) is a quite general relation since all the characteristic parameters for the separator and the discharge are contained in d_{min} and Q_{max} For eqn (25b) it is required that $Q < 0.923\ Q_{max}$, which coincides with the requirement $d < 2d_{min}$. Thus eqn (25a) is valid for all practical cases In Fig 7 the relationship between d/d_{min} and Q/Q_{max} as given by eqn (25b), is shown.

The separator used as an example in the previous part of the paper has a porosity $p = 0\ 65$ and a tortuosity factor of 1.3. It is obvious that at the 3 h discharge the introduction of this separator in the interelectrode space limits the acceptable thickness of the positive plate and markedly increases the weight and volume of the battery, compared with the design with a free electrolyte space adjacent to the positive plate. The limiting case of an ideal separator would be a porosity near to unity and with no tortuosity ($\theta = 1$)
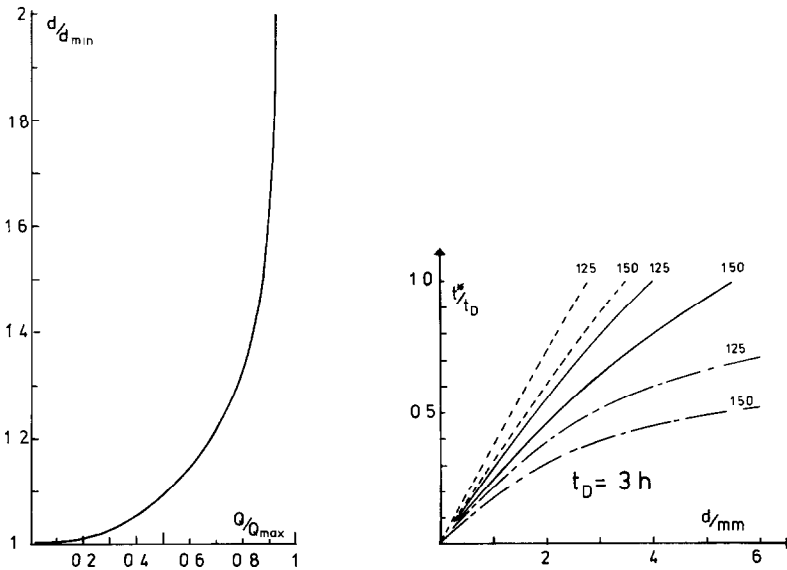
Fig 7 d/d_{min} as function of Q/Q_{max} according to eqn (25b)

Fig 8 t^*/t_D for $t_D = 3$ h and $Q = 125$ or 150 C cm^{-2} as indicated $----$, porosity 1 and no tortuosity, ———, medium porosity and tortuosity ($p = 0\ 85$ and $\theta = 1\ 16$), $-\cdot-$, separator as in Fig 4

This separator would only have the effect of excluding transport by convection and preventing electrolyte stratification. A "good" separator should have properties between these extremes, say $p = 0\ 85$ and $\theta = 1\ 16$

To illustrate the importance of the separator properties, t^*/t_D vs d plots are shown in Fig 8 for three separators with $t_D = 3$ h, two values of Q corresponding to 12 5 and 15 A h, and for a 180 cm^2 positive plate (two sides) The characteristic parameters for the 12.5 A h plate with each of the 3 separators is shown in Table 1

TABLE 1

Porosity (p)	0 65	0 85	1 0
Tortuosity (θ)	1 3	1 16	1 0
d_{mm}/mm	3 14	2 45	2 05
$Q_{max}/C\ cm^{-2}$	129	203	290
d/mm	8	2 8	2 2

$t_D = 3h$, $c^0_1 - c_{min} = 4\ 75$ mol dm^{-3}, $Q = 125$ C cm^{-2}, $r = 0\ 25$

The voltage loss in the separator

In the preceeding discussions, emphasis was placed on electrolyte depletion, not on the voltage losses caused by the hindered ionic transport through the separator It is shown below, however, that the voltage loss at room temperature is relatively small for constant current discharges at less than the "c_1" rate The voltage loss — considered as a positive figure — can be found as

$$\Delta\phi = -\int_0^d \frac{d\phi}{dx}\,dx \qquad (26)$$

Ohms law cannot be used directly due to the varying H$_2$SO$_4^-$ concentration, but using eqn (1) for H$^+$ and HSO$_4^-$ and the relation $\iota = F(J_+ - J_-)$ we get

$$\iota = -F(D_+ - D_-)\frac{dc}{dx} - (D_+ + D_-)\frac{F^2}{RT}c\frac{d\phi}{dx} \qquad (27)$$

isolating $d\phi/dx$ and using $\kappa = (c(D_+ + D_-)F^2/RT$, where κ is the local conductivity of H$_2$SO$_4$ in the separator, gives

$$\frac{d\phi}{dx} = -\frac{\iota}{\kappa} - \frac{RT}{F}(2t_+ - 1)\frac{dc}{c\,dx} \qquad (28)$$

or for $t_+ = 0\ 8$

$$\Delta\phi = \iota\int_0^d \frac{1}{\kappa}\,dx + 0\ 6\frac{RT}{F}\ln\frac{c_p}{c_n} \qquad (29)$$

The first term in eqn (29) is the ohmic potential loss taking into consideration that κ varies with c and, consequently, with x. The second term is a diffusion potential which, with the sign convention used, is always negative as $c_p < c_n$ This term diminishes the potential loss and when $c_p \to 0$, $\Delta\phi$ can reverse its sign.

The dependence of κ on c is nonlinear [14] Simonsson [2] gives the following empirical relation

$$c_1 > 0.2c^0_1, \kappa_1/\kappa^0_1 = 0.20 + 2.10c_1/c^0_1 - 1.3(c_1/c^0_1)^2$$

$$c_1 \leqslant 0.2c^0_1; \kappa_1/\kappa^0_1 = 2\ 84c_1/c^0_1$$

where c^0_1 is the initial acid concentration, 5 mol dm^{-3}. From Appendix A we have $c_1/c^0_1 = c/c^0$ and from eqn. (A8), $\kappa = \kappa_1 p/\theta^2$. Equation (29) can then be integrated numerically for a given t using eqn. (11) with $\iota = (1 - r)Q/t_D$ to determine c/c^0 for a given x and then eqn. (30) to find κ Figure 9 illustrates the outcome of this integration for a 1 h discharge with $Q = 125$ C cm^{-2}, $d = 0\ 4$ cm and values for the separator as in Figs. 3 - 6. The voltage loss has a reasonably low value It decreases as discharge proceeds and finally reverses its sign due to the influence of the second term in eqn. (29).
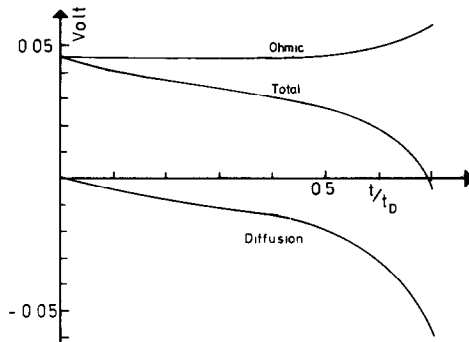

Fig 9 Voltage loss over separator region as function of t/t_D $Q = 125$ C cm^{-2}, $d = 0\ 4$ cm, $t_D = 1$ h, separator values as in Fig 4

Conclusion

The inclusion of a porous separator, which partially or completely occupies the interelectrode space will always decrease the energy density of the battery due to the added weight and volume. When the separator extends to the surface of the positive plate, however, transport due to convection is eliminated. This results in a parabolic concentration profile, which can decrease the interfacial acid concentration to such an extent that the amount of acid, and consequently the thickness of the separator, must be increased. At rated plate capacities of 100 C cm^{-2} or more, and at discharge rates less than 5 h, this may have a considerable influence on the energy density of the battery. In particular, it is very important to avoid low separator porosity

and high tortuosity — as expressed in the separator resistance — because it results in the transport remaining semi-infinite at the end of discharge This may happen if the discharge rate is too high or the plate capacity too large

According to the examples discussed in the paper, it appears that a separator intended for use in batteries for traction or EV use with immobilized electrolyte should have a porosity above 80% and a tortuosity factor less than 1 2

List of symbols

A	Cross sectional free area perpendicular to flux direction in separator
c	Amount of H_2SO_4 (mol) per unit separator volume
c^0	c in the fully charged condition
c_1	Concentration of H_2SO_4 in free acid in pore
c_{min}	Value of c_p at end of discharge
c_n	c at negative plate surface
c_p	c at positive plate surface
c_+, c_-	c for H^+ and HSO_4^-, respectively
D	Apparent diffusion coefficient for H_2SO_4 in separator
D_1	Diffusion coefficient for H_2SO_4 in free acid
D_+, D_-	Diffusion coefficient for H^+ and HSO_4^-, respectively
d	Interelectrode spacing Assumed equal to separator thickness
d_{min}	Separator thickness calculated for low discharge rates (equilibrium in separator)
F	Faraday's constant 96 487 C mol^{-1}
i	Current density in separator Positive for discharge
J_1	Flux density for species i
J	Flux density for H_2SO_4 in separator
J_1	Flux density for H_2SO_4 in separator pores
p	Porosity (void volume) in separator
Q	Rated specific capacity of positive plate C cm^{-2}
Q_{max}	Maximum capacity which can be obtained for infinite separator thickness
r	Amount of acid contained in the pores of the positive plate relative to total amount necessary to obtain Q
t	Time variable
t_D	Rated discharge time
t^*	Time when $c_p = c_{min}$
T	Dimensionless time $T = t/\tau$
t_+	Transport number for H^+
x	Spatial variable relative to separator surface
x_1	Spatial variable relative to flux direction in pore
z_1	Charge number
α	Boundary condition
ϕ	Galvani potential
ρ	Resistivity of separator filled with acid

θ Ratio between mean pore length and separator thickness Tortuosity factor

τ Time constant = d^2/D

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Appendix A

The transport equations in the porous separator

Let symbols without subscripts indicate values with the separator system as the reference and with the x-axis normal to the separator surface, and symbols with subscript "1" indicate values in the acid in the pores Eliminating ϕ in eqn (2) used for H^+ and HSO_4^- gives

$$J_1 = -D_1 \frac{dc_1}{dx_1} \tag{A1}$$

where D_1 is the diffusion coefficient of H_2SO_4 in free acid, and x_1 is parallel to the flux direction in the pores Consider a sheet of separator of thickness d. Excluding edge effects, all effective pores penetrate from one side of the sheet to the other Let the sum of all pore cross sectional areas per unit separator area be A The flux density in the separator is then

$$J = J_1 A \tag{A2}$$

The spatial variable, perpendicular to the separator surface, is

$$x = x_1/\theta \tag{A3}$$

where θ is the tortuosity factor, defined as the ratio of mean pore length (across the separator) to separator thickness. The concentration per unit separator volume is

$$c = c_1 p \tag{A4}$$

where p is the porosity.

Inserting in eqn. (A1) gives

$$J = \frac{A}{\theta p} D_1 \frac{dc}{dx} \tag{A5}$$

Excluding "dead end" pores the porosity can be found as

$$p = A\theta \tag{A6}$$

which, inserted in eqn. (A5), gives.

$$J = \frac{D_1}{\theta^2} \frac{dc}{dx} \Rightarrow D = D_1/\theta^2 \tag{A7}$$

Using a slightly different approach a similar relation for the mobility was found by Mackie *et al* [13]

Using the value for D defined above and $c = c_1 p$, eqn. (A4), and the following in the main paper holds.

The factor θ^2 can be found from resistance measurements on the acid filled separator The resistivity is

$$\rho = \frac{\theta}{A\kappa_1} = \frac{\theta^2}{p\kappa_1} \Rightarrow \frac{1}{\rho} = \frac{p\kappa_1}{\theta^2} \tag{A8}$$

where κ_1 is the conductance of the acid in the pores

For a commercial separator p is specified as $0\ 6 - 0\ 7$ and ρ as $2\ 8 - 5.6\ \Omega$ cm Using mean values and $\kappa_1 = 0.78\ (\Omega\ \text{cm})^{-1}$ [14], ($c_1 = 5\ \text{mol dm}^{-3}$) we get $\theta^2 = 2\ 12$, which gives $D = 0.77 \times 10^{-5}\ \text{cm}^2\ \text{s}^{-1}$ when D_1 is taken from eqn (19) for $c_1 = 1\ \text{mol dm}^{-3}$.

Appendix B

The acid in the positive plate pores

Assume a capacity of $0\ 12$ A h $= 432$ C per g of positive mass, and a density of 4 g cm^{-3}, then the capacity per cm^3 is 1728 C cm^{-3}. If the porosity is 0.55 then the acid content using 1.28 s.g. acid is 0.002 75 mol cm^{-3}. The electrode process in the positive plate consumes 1 mol HSO$_4^-$ per 2 F. Then the content of HSO$_4^-$ corresponds to 530.7 C cm^{-3}, or 31% of the plate capacity. Assuming that 80% of the acid can be used at discharge rates of $1 - 5$ h, r is estimated to be 0.25. For slow discharges, $r = 0.3$ can be used

The reasoning above assumes that HSO$_4^-$ is not transported out of the plate during discharge, which only holds if $t_+ = 1$ As $t_+ = 0.8$, however, $r = 0.25$ is considered a sufficiently good approximation.