

## TORTUOSITY

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### Summary

Tortuosity is defined for a particular separator model and basic equations are derived.

The deficiencies of an averaged tortuosity derived from steady state measurements are discussed, particularly as applied to non-steady-state situations. Two experimental procedures are outlined whereby more information can be obtained on the distribution of pore tortuosities in a given separator.

The difficulties of applying the tortuosity concept to membranes with fixed charges are outlined.

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### 1. Introduction

Tortuosity is an appropriate subject for a plenary lecture to open this Conference. Firstly, it is not possible to discuss the behaviour of separators and membranes in any depth without consideration of the effects of tortuosity. Secondly, despite its obvious importance and apparent simplicity in concept, tortuosity is not well understood and the scant literature is often misleading. There is an unfortunate tendency to allocate to tortuosity all the differences in behaviour between the real separator or membrane and some model chosen for simplicity or mathematical tractability. Under these circumstances tortuosity is often only an adjustable parameter used to improve the fit between the predictions of the model and the real data and is appropriate only for the conditions at which the match was made.

Much greater precision of thought is necessary if the concept of tortuosity is to become an aid rather than a hindrance in the comprehension of separator and membrane behaviour.

### 2. Model, definition of tortuosity and basic equations

For the purpose of this lecture it is assumed that a separator can be represented as an assembly of conducting pores. The substance which

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separates these pores, surrounds them, and, indeed, defines their shape and direction is ionically and electronically non-conducting. It is further assumed that the current flow in each pore is constant throughout its length and that the area of the pore normal to the direction of current flow is also constant throughout the length of the pore. While these latter assumptions are obviously oversimplifications they do lead to a very simple and convenient definition of tortuosity.

The current carried by an individual pore,  $i_n$ , is dependent upon the voltage drop across the separator,  $E$ , the specific conductivity of the electrolyte contained in the pore,  $\kappa$ , the area of the pore normal to current flow,  $A_n$ , and the length of the pore. This latter dependence is the one of significance; the current is unaffected by the particular meanderings of the pore and is dependent only on total length. Thus, the currents carried by the pores shown in Fig. 1 are identical provided that their lengths and all other parameters mentioned above are identical.

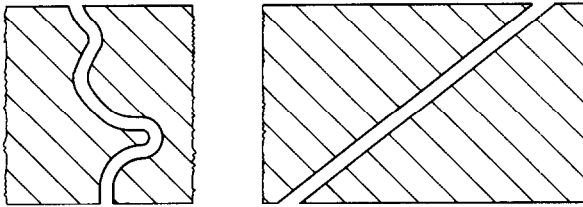


Fig. 1. Pores of identical tortuosity.

The ratio of the length of a pore to the thickness,  $L$ , of the separator is defined as the tortuosity of the pore,  $\theta_n$ . In other words, the length of the pore is  $\theta_n L$ .

$$i_n = \frac{E\kappa A_n}{\theta_n L} \quad (1)$$

The total current through all pores of tortuosity  $\theta_n$  is

$$I_n = \frac{E\kappa \bar{A}_n}{\theta_n L} \quad (2)$$

where  $\bar{A}_n$  is the sum of the areas normal to current flow of all pores of equal tortuosity,  $\theta_n$ . Now the volume fraction of all pores of equal tortuosity  $\theta_n$  is

$$V_n = \frac{\bar{A}_n \theta_n}{A} \quad (3)$$

where  $A$  is the geometric area of the separator. Combining eqns. (2) and (3)

$$I_n = \frac{E\kappa A V_n}{L\theta_n^2} \quad (4)$$

Now summing over pores for all tortuosities, the total current,  $I$ , through the separator is obtained

$$I = \frac{E\kappa A}{L} \sum_n \frac{V_n}{\theta_n^2}. \quad (5)$$

Substituting in eqn. (5) for the specific conductivity of the separator  $\bar{\kappa}$  ( $\bar{\kappa} = IL/EA$ ) the basic equation of this model is obtained

$$\frac{\bar{\kappa}}{\kappa} = \sum_n \frac{V_n}{\theta_n^2}. \quad (6)$$

If all the pores have identical tortuosity, eqn. (6) reduces to the simple expression,

$$\frac{\bar{\kappa}}{\kappa} = \frac{V}{\theta^2} \quad (7)$$

where  $V$  is the volume fraction of pores and  $\theta$  is the tortuosity of all pores.

Usually all pores do not have the same tortuosity but eqn. (7) is still used to derive a tortuosity from measured values of  $\bar{\kappa}$  and  $\kappa$ . Under these circumstances the derived tortuosity is an "averaged" value which may be given the symbol  $\bar{\theta}$ . Thus

$$\frac{1}{\bar{\theta}^2} = \frac{1}{V} \sum_n \frac{V_n}{\theta_n^2}. \quad (8)$$

An equation analogous to eqn. (6) may be derived for diffusion. Thus

$$\frac{\bar{D}}{D} = \sum_n \frac{V_n}{\theta_n^2}. \quad (9)$$

### 3. Pareto distribution

In order to use eqn. (6) information is needed on the distribution of tortuosities in a separator. It would be helpful mathematically if a continuous distribution could be assumed, and the Pareto distribution has been suggested [1] as a possible candidate. It is of the right form in that the Pareto distribution would allow  $\theta_n$  to be continuously variable from unity to infinity.  $\theta_n$  equals unity for a pore normal, throughout its length, to the separator surface and infinity for a pore of infinite length.

In the present context the Pareto distribution may be written

$$\int_1^{\theta_n} V_n d\theta_n = V(1 - \theta_n^{-\alpha}) \quad (10)$$

where  $\alpha$  is a structure factor which is selected to match the character of a particular separator. As  $\theta_n$  no longer has discrete values but is continuously

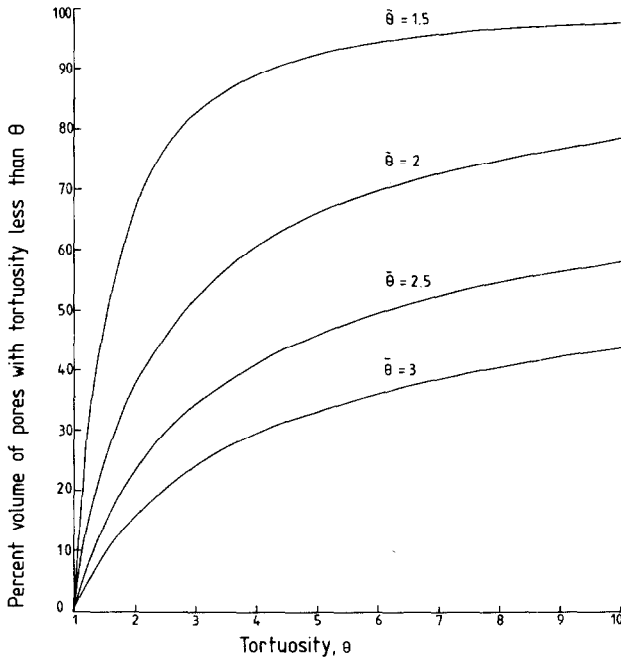


Fig. 2. Pareto model, cumulative pore distributions.

variable, the definition of  $V_n$  must be changed slightly.  $V_n$  is now the volume fraction of pores with tortuosities between  $\theta_n$  and  $\theta_n + \delta\theta_n$ .

Figure 2 shows cumulative pore distributions, based on a Pareto model, for separators having averaged tortuosities (eqn. (8)) of 1.5, 2, 2.5 and 3. Clearly, the Pareto model represents a separator as having pores with a wide range of tortuosities.

The Pareto model can be used to calculate the contribution pores of various tortuosities make to the total conductivity. This is shown in Fig. 3. Comparison of Figs. 2 and 3 illustrates dramatically the overriding importance of the contribution of pores of low tortuosity to conductivity. For example, for averaged tortuosities of 1.5, 2.0, 2.5 and 3, 90% of the conductivity is contributed by 64%, 45%, 32% and 23%, respectively, of the pore volume.

#### 4. Analysis of pore tortuosity

Although the Pareto model has been used to illustrate the predominant contribution to conductivity of pores of low tortuosity, the effect is not dependent upon the assumption of such a model.

Consider a hypothetical separator having a pore volume fraction of 0.6 with half of this volume fraction consisting of pores of tortuosity 1.5 and the other half of pores of tortuosity 4. By eqn. (6) it is a simple matter to

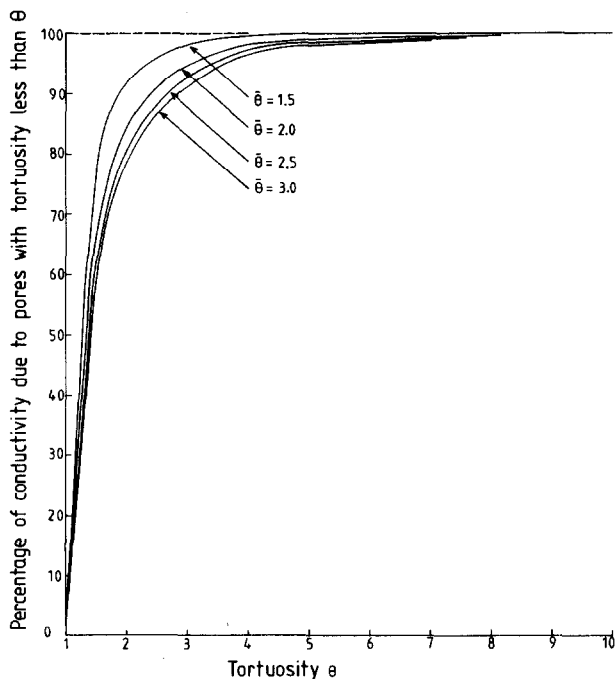


Fig. 3. Pareto model, cumulative conductivity curves.

calculate that the pores of tortuosity 4 contribute only 12% to the overall conductivity even though they occupy half of the pore volume. If this half had also a tortuosity of 1.5, conductivity would be increased by 75%. Such potential improvements are not usually recognised, however, because only an averaged tortuosity is obtained from steady state measurements. For the hypothetical separator now being considered, the averaged tortuosity calculated using eqn. (8) is 2.

Steady state measurements cannot distinguish between a separator in which all the pores have a tortuosity of 2 and one in which half the pore volume has a tortuosity of 1.5 and the other half a tortuosity of 4.0. The separator manufacturer is thus unaware in the latter case that half of the pore volume is contributing little to conductivity and that a substantial improvement in conductivity is possible if he could make changes to convert all the pore volume into a tortuosity of 1.5. What is needed is a means of recognising the presence in a separator of pores of high tortuosity.

A method, diffusion ingress, is available in principle, although it does not appear to have been tried. The experimental procedure is very simple. Pieces of separator full of water are immersed in a well stirred solution of excess electrolyte of known concentration. After various times pieces are removed and the amount of electrolyte that has diffused in is determined. The experiment yields the amount diffused in,  $M_t$ , after time  $t$  as a fraction of the amount diffused in after infinite time,  $M_\infty$ .

The equations governing this behaviour [2] are easily modified for the present situation. Thus

$$\frac{M_t}{M_\infty} = 1 - \sum_n \frac{V_n}{V} \sum_{m=0}^{\infty} \frac{8}{(2m+1)^2 \pi^2} \exp\left(-\frac{D(2m+1)^2 \pi^2 t}{\theta_n^2 L^2}\right) \quad (11)$$

where  $D$  is the diffusion coefficient for the electrolyte. Numerical data appropriate to eqn. (11) are available in ref. 2 (Fig. 4.6, curve labelled 0). These data have been used to compare the diffusion ingress curves for a separator with pores of a single tortuosity, 2 (separator A), with one which has an averaged tortuosity of 2 but actually consists of equal pore volumes of tortuosities 1.5 and 4.0 (separator B). The comparison is shown in Fig. 4. The presence of pores of high tortuosity in separator B is clearly revealed by the continuing diffusion ingress at long times. Thus, non-steady-state experiments of this type can distinguish between separators of identical averaged tortuosity but with different distributions of pore tortuosity.

The spectrum of pore tortuosities present in a separator is probably continuous. By making an arbitrary choice of discrete tortuosities, however, it is possible to analyse a diffusion ingress curve in terms of the assumed tortuosities. For the purpose of illustration it has been assumed that both

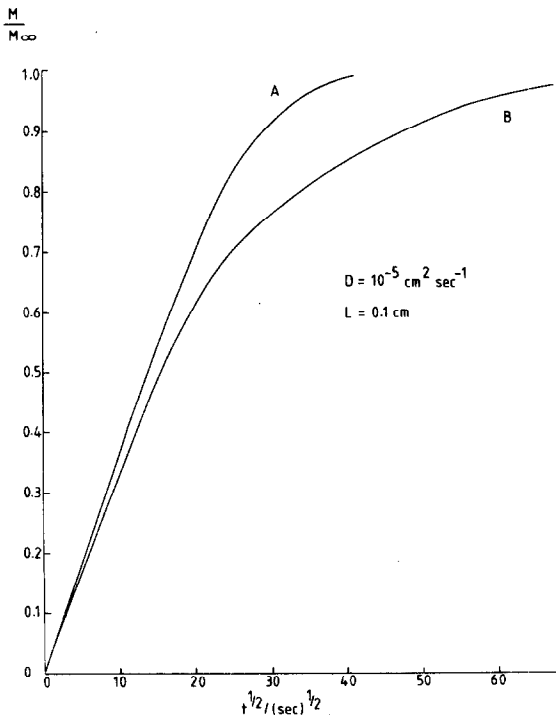


Fig. 4. Diffusion ingress. Separator A, all pores have tortuosity 2; separator B, averaged tortuosity 2, pore volume equally divided between pores of tortuosity 1.5 and 4.0.

steady state and non-steady-state behaviour of a real separator may be represented by a hypothetical separator consisting of various volume fractions of the following tortuosities: 1.0, 1.4, 2.0, 2.8, 4.0 and 5.6. The principle of the analysis is then to choose the various volume fractions so that the theoretical diffusion ingress curve for the hypothetical separator closely matches the experimental curve for the real separator.

Figure 5 shows the theoretical diffusion ingress curves for hypothetical separators having all their pores with a single tortuosity of 1.0, 1.4, 2.0, 2.8, 4.0 or 5.6. A possible procedure is then as follows: the experimental diffusion ingress curve for the real separator is examined to determine the increase in  $M_t/M_\infty$  between  $\sqrt{Dt}/L$  values of 2.1 and 3.0.

Let this be 
$$\exp \left[ \Delta \frac{M_t}{M_\infty} \right]_{\sqrt{Dt}/L, 2.1/3.0}$$

Figure 5 is examined to determine the theoretical increase in  $M_t/M_\infty$  for a separator in which all the pores have a tortuosity of 5.6.

Let this be 
$$\theta = 5.6 \left[ \Delta \frac{M_t}{M_\infty} \right]_{\sqrt{Dt}/L, 2.1/3.0}$$

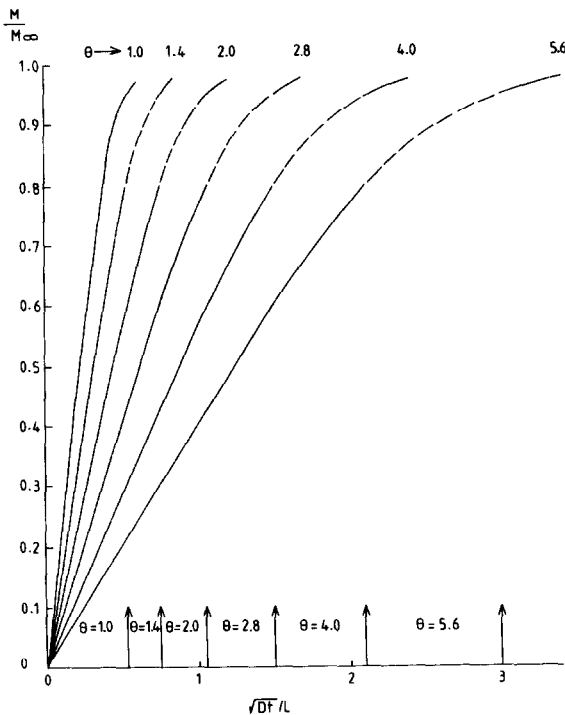


Fig. 5. Diffusion ingress with pores of a single tortuosity.

$$\text{Then } \frac{\exp \left[ \Delta \frac{M_t}{M_\infty} \right]_{\sqrt{Dt}/L, 2.1/3.0}}{\theta = 5.6 \left[ \Delta \frac{M_t}{M_\infty} \right]_{\sqrt{Dt}/L, 2.1/3.0}} = \frac{V_{5.6}}{V}$$

where  $V_{5.6}$  is the deduced volume fraction of pores with tortuosity 5.6.

A second experimental curve is then derived by subtracting from the original experimental curve the contribution due to the pores of tortuosity 5.6. This is done by multiplying the ordinates for the theoretical curve for a tortuosity of 5.6 shown in Fig. 5 by  $V_{5.6}/V$  and subtracting the results from the ordinates of the original experimental diffusion ingress curve.

$V_{4.0}/V$  is then derived similarly by comparing the increase in  $M_t/M_\infty$  between  $\sqrt{Dt}/L$  values of 1.5 and 2.1 for the second experimental curve with the theoretical curve for a tortuosity of 4.

The contribution of pores of tortuosity 4 is then removed from the second experimental curve and the increase in  $M_t/M_\infty$  examined between  $\sqrt{Dt}/L$  values of 1.05 and 1.5 to find the volume fraction of pores of tortuosity 2.8 and so on.

The choice of  $\sqrt{Dt}/L$  values is determined by the requirement that diffusion ingress of the next lower tortuosity class shall be 95% complete at the lower  $\sqrt{Dt}/L$  value, and for the tortuosity class under examination shall be 95% complete at the higher  $\sqrt{Dt}/L$  value. This leads to the  $\sqrt{Dt}/L$  values shown in Table 1.

The highest tortuosity class can, of course, be examined up to  $\sqrt{Dt}/L$  values of infinity and the lowest down to  $\sqrt{Dt}/L$  equals zero.

The volume fractions so derived can, of course, be given some final adjustment so that:

(i) their use in eqn. (11) gives a theoretical diffusion ingress which matches the experimental result as closely as possible,

$$(ii) V_{5.6} + V_{4.0} + V_{2.8} + V_{2.0} + V_{1.4} + V_{1.0} = V$$

and

$$(iii) \frac{V_{5.6}}{5.6^2} + \frac{V_{4.0}}{4.0^2} + \frac{V_{2.8}}{2.8^2} + \frac{V_{2.0}}{2.0^2} + \frac{V_{1.4}}{1.4^2} + \frac{V_{1.0}}{1^2} = \frac{V}{\bar{\theta}^2}$$

where  $\bar{\theta}$  is the averaged tortuosity determined by a steady state method.

While the diffusion ingress method should be satisfactory for determining the volume fractions of pores of high tortuosity, thus highlighting scope for separator improvement, it is open to criticism on the grounds that the volume fractions of pores of low tortuosity, and these are the ones which control steady state behaviour, are only obtained after a succession of computations and therefore may be in error. Fortunately there is a complementary experiment in which the volume fractions are determined in the opposite order (*i.e.*, the volume fractions of the lower tortuosity pores are determined first).

The experiment which may be called diffusion breakthrough is a little more difficult experimentally. The separator is initially filled with water and



TABLE 1

Diffusion ingress method

Tortuosity class	Examine between $\sqrt{Dt}/L$ values of
5.6	2.1 , 3.0
4.0	1.5 , 2.1
2.8	1.05 , 1.5
2.0	0.75 , 1.05
1.4	0.53 , 0.75
1.0	0.38 , 0.53

the solutions on either side of it are kept at zero concentration and at a pre-determined level. The flux of electrolyte  $J_t$  through the separator and into the solution of zero concentration, expressed as a fraction of the steady state diffusion flux  $J_\infty$ , is measured as a function of time. The equations governing this behaviour are readily deduced from the literature [3].

$$\frac{J_t}{J_\infty} = \sum_n \frac{V_n \bar{\theta}^2}{V \theta_n^2} \left[ 1 + 2 \sum_{m=1}^{\infty} (-1)^m \exp\left(-\frac{Dm^2 \pi^2 t}{\theta_n^2 L^2}\right) \right]. \quad (12)$$

Figure 6 compares the diffusion breakthrough curves for a separator with pores of a single tortuosity 2 (separator A) with one which has an

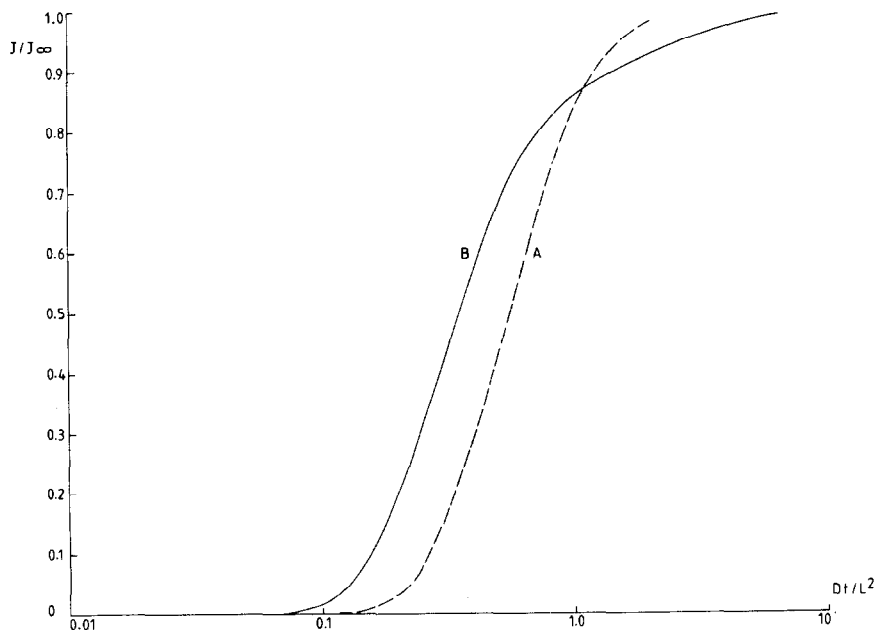


Fig. 6. Diffusion breakthrough. Separator A, all pores have tortuosity 2; separator B, averaged tortuosity 2, pore volume equally divided between pores of tortuosity 1.5 and 4.0.

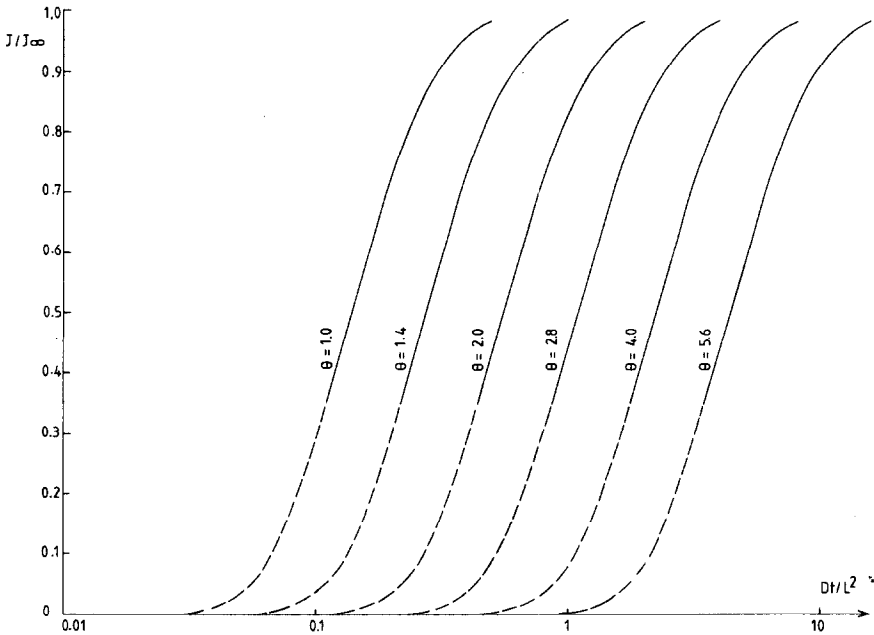


Fig. 7. Diffusion breakthrough with pores of a single tortuosity.

averaged tortuosity of 2 but actually consists of equal pore volumes of tortuosities 1.5 and 4 (separator B). There is a clear distinction between them.

Figure 7 shows the theoretical diffusion breakthrough curves for hypothetical separators each having pores of only a single tortuosity of 1.0, 1.4, 2.0, 2.8, 4.0 or 5.6. In a similar manner to the procedure already described for diffusion ingress, an experimental diffusion breakthrough curve can be analysed on the basis of the theoretical curves given in Fig. 7. In this case the volume fraction of pores of tortuosity 1.0 is first determined by comparing the value of  $J_t/J_\infty$  at the  $Dt/L^2$  value of 0.11 for the experimental curve with the theoretical value given in Fig. 7. The contribution of the derived volume fraction of pores of tortuosity 1.0 is then eliminated from the experimental diffusion breakthrough curve and the volume fraction of pores of tortuosity 1.4 next derived by comparison of  $J_t/J_\infty$  at the  $Dt/L^2$  value of 0.22 with the appropriate theoretical curve.

The choice of  $Dt/L^2$  values shown in Table 2 is based on the requirement that diffusion breakthrough of the next higher tortuosity class shall be only 5% of its maximum value.

## 5. Battery implications

Separator tortuosities are almost always determined by steady state methods. From the foregoing it is clear that averaged tortuosities derived in

TABLE 2

Diffusion breakthrough method

Tortuosity class	Examine at $Dt/L^2$ values of
1.0	0.11
1.4	0.22
2.0	0.44
2.8	0.88
4.0	1.76
5.6	3.52

this way may not be useful in predicting or understanding separator behaviour in non-steady state conditions. Thus two separators may behave identically on an electrical resistance test but show quite different performances on engine starting. For a better comprehension of non-steady-state behaviour, analysis of the separator in terms of pores of various tortuosities is necessary.

Lest it be thought that batteries are rarely used in non-steady-state conditions a few civilian examples follow.

Engine starting	— lead-acid and nickel-cadmium batteries
Electronic camera controls	— silver and mercury button cells
Electronic photoflash	— alkaline manganese batteries
Cassette recorders	— Leclanché and alkaline manganese batteries
Fast charging	— nickel-cadmium batteries
Smoke alarms	— alkaline manganese batteries.

## 6. Membranes

The discussion so far has been concerned with separators in which the electrolyte contained in the pores is identical with the external solution. The separator substance behaves only as an obstacle. It influences the shape and direction of the pores but not the nature of the electrolyte contained within them. Under these circumstances it is a simple matter to determine an averaged tortuosity from steady state measurements by means of eqns. (8) and (6) or (9). Such tortuosities are useful in steady state situations because they apply to both diffusion and conductivity and to any electrolyte at any concentration. In other words to situations other than those in which they were derived.

There is, however, frequent use made in the literature of the same equations to derive a so-called tortuosity for membranes which contain internal fixed charge groups. Internal fixed charge groups cause the concentrations of ions in the membrane to differ from those in the external

solution. If the concentration of cations is enhanced relative to the external solution, the concentration of anions is diminished and *vice versa*. The nature of the electrolyte, 1:1, 1:2, 2:1, 2:2, is important, as is its concentration. The relationship between diffusion and conductance is complex, *e.g.*, in dilute external solutions a membrane may permit ionic conduction while preventing diffusion. The internal volume fraction probably varies with the nature and concentration of the external electrolyte.

Because of the above circumstances, a tortuosity determined from conductance measurements made with and without a membrane has no physical reality and is of little use in predicting behaviour in situations different from those in which it was determined.

The starting point for understanding membrane behaviour must be a knowledge of the concentrations of mobile ions in the membrane. Even this, however, is only partially helpful, as their mobilities are, in general, not predictable from mobilities in the external solution. This is because the fixed charge groups polarise the membrane medium such that the centre of gravity of the counter-ions is closer to the fixed charge groups than the centre of gravity of the co-ions.

In such a complex situation it would be useful to have an independent measurement of tortuosity. This can be attempted with a species that is less affected by the membrane structure than ions. A possible choice is water. By use of isotopic species, self diffusion coefficients can be determined in the membrane and compared with external solution to determine an averaged tortuosity. This has been done only rarely and, even so, is not without criticism, as the self-diffusion coefficient depends upon the viscosity of the medium. The implicit and probably incorrect assumption is that the membrane structure does not affect viscosity. Since viscosity inside the membrane will be difficult if not impossible to assess, however, it may be convenient for membranes to use a tortuosity which combines the viscosity change with the obstacle effect caused by the membrane.

## Acknowledgements

The author thanks Dr W. C. Maskell and Mr J. H. J. Mallaby for helpful discussions during the preparation of this lecture, and the Directors of the Berc Group Limited for permission to publish.

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