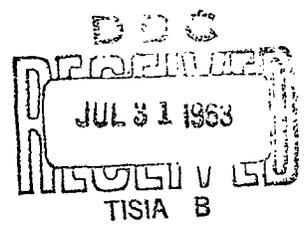
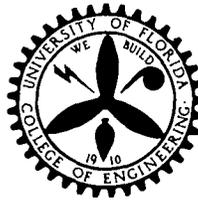


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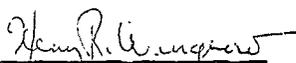
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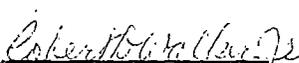
Mass Transfer In Porous Gas Diffusion Electrodes.
III. The Effect on Mass Transfer of Pore Tortuosity and Constriction.

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ENGINEERING AND INDUSTRIAL EXPERIMENT STATION

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1.0 SUMMARY

The effects of tortuosity and convergence on mass transfer in pores are examined as they relate to current densities supportable by mass transport in porous gas diffusion electrodes. Both of these factors are basically empirical constants defined to give the experimental value of mass flux using the bulk diffusivity of the diffusing species. The relationship between the effective diffusivity, D_e , and other factors is given by

$$D_e = D_b \left(\frac{\epsilon \delta}{\tau} \right) \quad (1)$$

Theoretical models of various kinds have been examined, but the conclusion is that the predictions are of doubtful value and experimental determination of the effective diffusivity is the most reliable method.

The current density is related to tortuosity and constriction by the following relation

$$\frac{i}{i_{\max}} \propto \frac{\delta}{\tau} \quad (2)$$

To illustrate simply, the effect of pore tortuosity and constriction, if the tortuosity, τ , has a value of 5.0 and the convergence factor, δ , has a value of 0.5, the current density supportable by mass transport is reduced to 10 per cent of the value attainable in a straight pore of the same nominal length and of uniform cross-section.

2.0 INTRODUCTION

For mathematical simplicity, most models of porous media are postulated as a bundle of parallel, straight, cylindrical pores of length equal to the thickness of the porous medium. This idealization is never reached in porous media, for the diffusion path in most porous materials is tortuous. Unfortunately, the exact path is very difficult to identify, and experimenters have usually resorted to the practice of defining a tortuosity factor, τ , which is, in effect, a corrected pore length adjusted to bring experimental results into agreement with theoretical calculations. Likewise, the pores in most porous media consist of alternating expansions and contractions rather than pores of uniform cross-section. For this reason it is necessary to define an effective diffusivity, D_e , which is less than the bulk diffusivity, D_b .

For these reasons a realistic picture of the flow paths in a porous solid is that of random distribution of irregularly shaped cavities connected to one another so as to make tortuous channels. Therefore, the medium controls the path of flow in a random manner, and it is this difference between the simple model and the complex case observed in practice that tortuosity and constriction factors attempt to satisfy.

3.0 DISCUSSION OF PORE TORTUOSITY

Since one of the idealizations in the study of porous media is the assumption that the pores are straight, investigators have used an effective pore length, or effective fluid particle path length. The ratio of this quantity to the thickness of the medium (1) is known as the tortuosity. This relationship is shown by equation 3.0-1 where L_e is effective pore length, L is thickness of medium, and τ is tortuosity.

$$\tau = L_e/L \quad 3.0-1$$

Other authors (2) have related τ to measured quantities such as the porosity or volume fraction of voids, ϵ , the experimental diffusivity through the medium, D_e , and the bulk diffusivity, D_b , as shown in equation 3.0-2.

$$\tau = \frac{\epsilon}{D_e/D_b} \quad 3.0-2$$

There is considerable difference of opinion as to the value which should be accepted for τ in equation 3.0-1. Carman (1) gives his own and two other opinions on this value as $(2)^{\frac{1}{2}} = 1.41$, $(\frac{\pi}{2})^{\frac{1}{2}} = 1.26$, and 1.5.

Equation 3.0-2 is obtained by direct experimentation; hence the value of τ is different for each medium. It is not certain that media of the same porosity or effective diffusivity, have the same values of τ , so that both must be measured. However, once D_e is known, the practical need for τ disappears since fluxes may be calculated if one knows the effective diffusivity.

Attempts have been made to relate τ to the ratio of electrical conductivity of media saturated with electrolyte to that of the conductivity of the pure electrolyte (1), but there is some doubt as to how this related to the ratio L_e/L .

Scheidegger (3) gives the following relationship between the permeability, k , the porosity, ϵ , and the specific surface area, S .

$$k = \frac{\epsilon^3}{2S^2} \quad 3.0-3$$

He then states that since equation 3.0-3 does not correctly represent the observed relation between the various factors, therefore, any numerical factors are "lumped together" in a "tortuosity" τ to give

$$k = \frac{\epsilon^3}{\tau^2 S^2} \quad 3.0-4$$

In general then, the tortuosity factor is a constant of proportionality. Some authors have endeavored to give it physical significance while others have been content to leave it as an experimentally determined factor. It appears reasonable to try to give τ physical significance similar to equation 3.0-1, but when values of $\tau \geq 10$ are observed this is difficult to visualize (1).

Some attempt (4) has been made to learn (by the application of statistical techniques) how the random properties of a medium affect the path of a fluid through it. This would give some idea of actual path length, and τ from equation 3.0-1 could then be calculated. However, it should be noted that agreement between experimental observations and calculated quantities may possibly require the introduction of another constant.

4.0 DISCUSSION OF PORE CONVERGENCE

The tortuosity derived from equation 3.0-2 has been found to be quite high for tableted or extruded porous media, with average values around 10 to 12. Petersen (2) explained this high tortuosity as a contribution due to pore constriction and expansion, and the redefined tortuosity in a porous solid as

$$\tau = \frac{\epsilon \delta}{D_e / D_b} \quad 4.0-1$$

He calls δ the convergence factor.

As his model Petersen takes hyperbolas of revolution about Z, where Z is the length of the pore. He then solves the steady-state Laplace equation for one section. Using the bulk diffusivity, D_b , the flux is computed. The quantity D_e is defined as the value required to give that same flux in a smooth cylindrical pore of radius r_{avg} (5), and

$$r_{avg} = \frac{2v}{S} \quad 4.0-2$$

where v is total pore volume, and S is internal surface area. He then concludes that

$$\frac{D_e}{D_b} = \delta \quad 4.0-3$$

for any number of constriction units in series (5).

The convergence factor, δ , is a function of the pore constriction, and it varies from 1 to about 0.33 when the ratio of area at

pore entrance to the area of the pore constriction varies from 1 to 25.

Since τ from equation 4.0-1 is measured experimentally it makes little practical difference if τ or $(\tau)(\delta)$ is the quantity measured. Therefore, while the postulate of a convergence factor may aid our understanding of the actual process, it does not reduce the amount of effort required to obtain useful data for calculation purposes.

5.0 EFFECT OF PORE TORTUOSITY AND CONVERGENCE ON MASS TRANSFER IN POROUS SOLIDS

Both tortuosity and/or constriction reduce the mass flux through the pores; therefore, the more uniform the pores can be made the greater the flux through them. The effects of tortuosity and convergence are shown graphically in Figure 1.

As an example of the reduction of current density due to tortuosity and constriction consider the following case. Current density is proportional to diffusivity so that equation 5.0-1 applies.

$$\frac{i}{i_{\max}} \propto \frac{D_e}{D_b} \propto \frac{\delta}{\tau} \quad 5.0-1$$

With a convergence factor of 0.5 and a tortuosity of 4, the current density is 12.5% of the maximum current density obtainable. A plot of equation 5.0-1 is shown in Figure 1.

Previous work at the Power Supply Laboratory, University of Florida (6,7) has shown that for an increase in pore length by 10 the current density is reduced to approximately one-third of its original value. However, in this work the radius of the pore was increased to maximize the current density. If the pore radius is kept constant at 1.8×10^{-6} cm (6) then an increase in pore length by a factor of 10 will reduce the current density from 1.45 amps/cm^2 (6) to 0.145 amps/cm^2 .

Similarly the effect of non-constant cross-section would be to reduce the current density even more. For example, if the optimum pore radius is used as in equation 4.0-2 and we have a convergence factor of 0.5, the current density for a semi-infinite annulus would be only $7.25 \times 10^{-2} \text{ amps/cm}^2$ or 7.25 millamps/cm² with a tortuosity of 10.

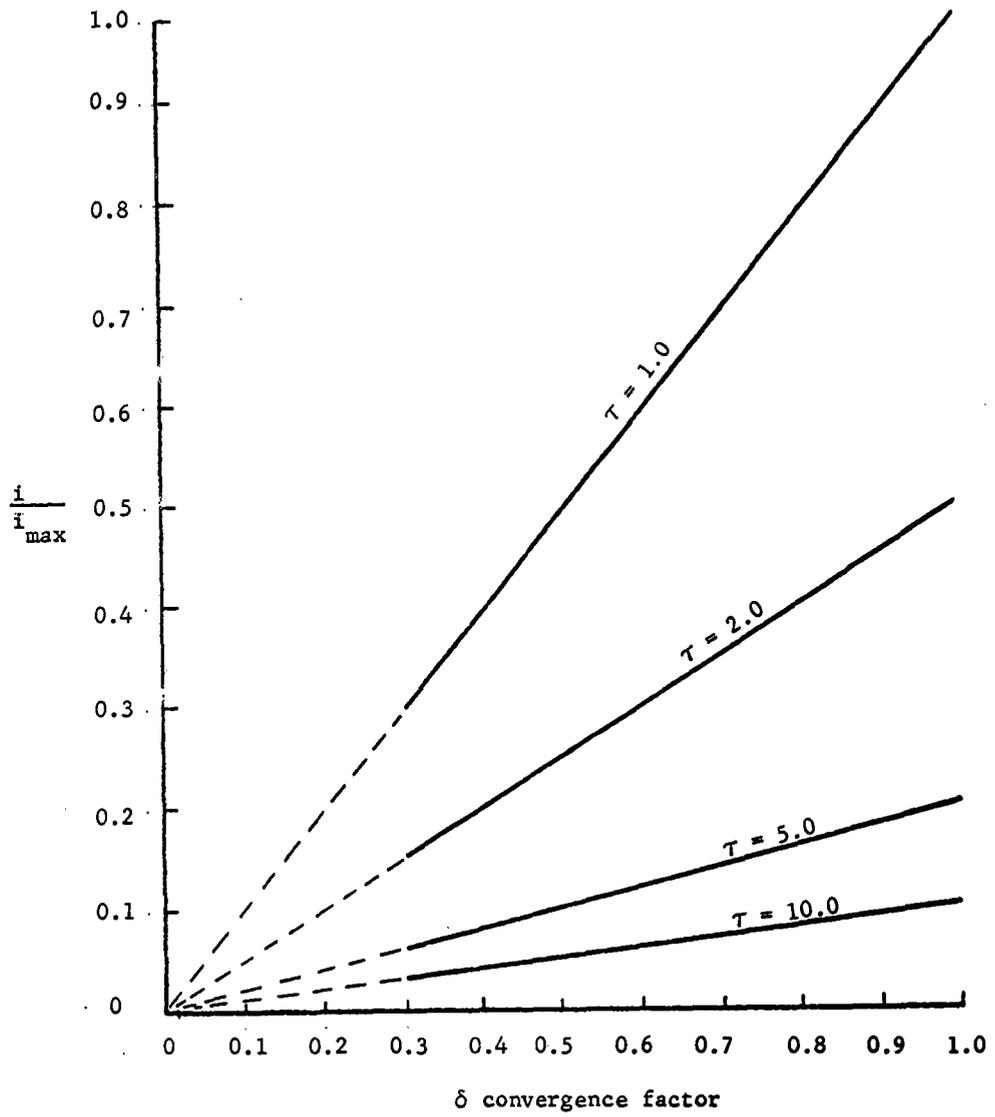


Figure 1

Effect of Tortuosity and Convergence on Mass Transfer in a Pore

In present-day porous gas diffusion electrodes it seems unlikely that values of the tortuosity can be less than 2. More realistic values would appear to be $\tau \sim 5.0$ and $\delta \sim 0.5$. From Figure 1, it may be seen that the current density supportable by mass transport in such a pore would be only about 10 per cent of the current density supportable in a straight pore of the same nominal length having a uniform circular cross-section.

SYMBOLS

D_b	bulk diffusivity of gas, cm^2/sec .
D_e	experimental diffusivity through medium, cm^2/sec .
i	current density, ma/cm^2
k	permeability, cm^{-4}
L	thickness of medium, cm
L_e	effective pore length, cm
S	specific surface area, cm^2/cm^3
α	proportional to
δ	convergence factor
ϵ	porosity
π	numerical constant 3.1416
τ	tortuosity

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