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#### THE AUTHOR

Mike Williams, born and bred in Wisconsin, took the convenient but fortunate educational route through Madison. The B.S. led to a summer job at Los Alamos which stimulated his interest in rheology, and he returned to Madison to study continuum modeling with Bob Bird. After getting his Ph.D. in 1964, Mike spent a year at the University of Oregon with Marshall Fixman and focused on molecular rheology. Since arriving at Berkeley, he has tried to synthesize these two research interests and has also dabbled in drag reduction, block copolymer thermodynamics, and flow-induced blood damage.

His extracurricular activities include a ridiculous degree of participation in baseball and tennis and a fannish interest in all sports, but most of his outside time is engaged in career guidance work with high school students.

#### JOURNAL REVIEW

# Porous-Electrode Theory with Battery Applications

Developments in the theory of flooded porous electrodes are reviewed with regard to simulation of primary and secondary batteries, adsorption of ions and double-layer charging, and flow-through electrochemical reactors.

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Porous electrodes have numerous industrial applications primarily because they promote intimate contact of the electrode material with the solution and possibly a gaseous phase. Specific factors are as follows:

1. The intrinsic rate of the heterogeneous electrochemical reaction may be slow. A porous electrode can compensate for this by providing a large interfacial area per unit volume (for example,  $10^4 \text{ cm}^{-1}$ ).
2. Double-layer adsorption constitutes the basis for novel separation processes involving cycling of the electrode potential. Just as in conventional fluid-solid adsorption, a high specific interfacial area is desirable.
3. Important reactants may be stored in the solution in close proximity to the electrode surface by means of porous electrodes. This permits sustained high-rate discharge of the lead-acid cell.
4. A dilute contaminant can be removed effectively with a flow-through porous electrode. The proximity of the flowing stream to the electrode surface is again important.
5. Similar arguments apply to nonconducting reactants of low solubility. Then another solid phase (as in batteries) or a gas phase (as in fuel cells) may be incorporated into

the system, or the reactants may be dissolved and forced through a porous electrode.

6. The compactness of porous electrodes can reduce the ohmic potential drop by reducing the distance through which current must flow. This has obvious advantages in reducing the losses in batteries and fuel cells. It may also permit operation without side reactions by providing potential control for the desired process.

If porous electrodes were trivially different from plane electrodes, there would be no motivation for their separate study. But here inherent complications arise because of the intimate contact of electrode and solution—the ohmic potential drop and the mass transfer occur both in series and in parallel with the electrode processes, with no way to separate them. One needs to develop an intuitive feeling for how and why the electrode processes occur nonuniformly through the depth of the electrode. Finally, we seek methods for designing a porous electrode for a particular application in such a way as to maximize the efficiency.

Electrodes with two fluid phases are excluded from consideration here. Gas electrodes for fuel cells are reviewed

by Chizmadzhev et al. (1971) and by Bockris and Srinivasan (1969) among others. The present article is also more concerned with macroscopic porous-electrode theory than with the detailed morphology and reaction mechanisms of particular chemical systems (see, for example, Burbank et al., 1971; Milner and Thomas, 1967) or with the growth of crystals or layers of insoluble products (see Hoar, 1959; Young, 1961; Vermilyea, 1963).

With these exclusions, a broad subject area remains. Battery electrodes illustrate an industrially important application of porous-electrode theory. Flow-through porous electrodes have some promise for recovery and removal of electropositive metals (Ag, Au, Cu, Hg, Pb) from dilute solutions, for electro-organic synthesis, and for oxidation of unwanted organic pollutants and surfactants. Transient double-layer charging and adsorption are of interest in the determination of the internal area of porous electrodes, in some separation processes, and in the interpretation of impedance measurements on porous electrodes.

Fundamentals of electrochemical thermodynamics, kinetics, and transport processes are not explained at length. We build here on earlier expositions of these subjects (see, for example, Newman, 1967, 1973).

The earlier reviews of Grens and Tobias (1964), Posey (1964), and de Levie (1967) are relevant and have been consulted particularly in regard to the early Russian literature. See also Gurevich et al. (1974).

## MACROSCOPIC DESCRIPTION OF POROUS ELECTRODES

Porous electrodes consist of porous matrices of a single reactive electronic conductor or mixtures of solids which include essentially nonconducting, reactive materials in addition to electronic conductors. An electrolytic solution penetrates the void spaces of the porous matrix. At a given time, there may be a large range of reaction rates within the pores. The distribution of these rates will depend on physical structure, conductivity of the matrix and of the electrolyte, and on parameters characterizing the electrode processes themselves.

In order to perform a theoretical analysis of such a complex problem, it is necessary to establish a model which accounts for the essential features of an actual electrode without going into exact geometric detail. Furthermore, the model should be described by parameters which can be obtained by suitably simple physical measurements. For example, a porous material of arbitrary, random structure can be characterized by its porosity, average surface area per unit volume, volume-average resistivity, etc. Similarly, one can use a volume-average resistivity to describe the electrolytic phase in the voids. A suitable model would involve averages of various variables over a region of the electrode small with respect to the overall dimensions but large compared to the pore structure. In such a model, rates of reactions and double-layer charging in the pores will have to be defined in terms of transferred current per unit volume.

A number of early and recent models represent the structure with straight pores, perpendicular to the external face of the electrode, and a one-dimensional approximation is introduced and justified on the basis of the small diameter of the pore compared to its length. As de Levie (1967) has pointed out, the mathematical equations to treat are essentially identical with those of the macroscopic model although a parameter such as the diffusion coefficient has a different interpretation. We shall prefer to speak in terms of the macroscopic model. The model set forth by Newman and Tobias (1962) has elements which can be found in the earlier work of Coleman (1946), Daniel-Bek (1948), Ksenzhek and Stender (1956a, b), and Euler and

Nonnenmacher (1960). Refinements (Posey and Morozumi, 1966; Johnson and Newman, 1971, for example) permit the treatment of double-layer charging and make clearer the applicability to flow-through electrodes and electrodes with time-dependent structural parameters.

## Average Quantities

In this macroscopic treatment, we disregard the actual geometric detail of the pores. Thus, we can define a potential  $\Phi_1$  in the solid, conducting matrix material and another potential  $\Phi_2$  in the pore-filling electrolyte. These quantities, and others to be defined shortly, are assumed to be continuous functions of time and space coordinates. In effect, the electrode is treated as the superposition of two continua, one representing the solution and the other representing the matrix. In the model, both are present at any point in space.

Dunning (1971) has included an extensive discussion of average quantities and the derivation of certain equations in a manner designed to clarify the nature of the averages used.

Averaging is to be performed in a volume element within the electrode. The porosity is the void volume fraction  $\epsilon$  within the element, and this is taken here to be filled with electrolytic solution. The element also contains representative volumes of the several solid phases which may be present. Let  $c_i$  be the solution-phase concentration of species  $i$ , averaged over the pores. The superficial concentration, averaged over the volume of both matrix and pores, is thus  $\epsilon c_i$ . For flow-through electrodes,  $c_i$  is the preferred average concentration because it is continuous as the stream leaves the electrode. Furthermore,  $c_i$ , rather than  $\epsilon c_i$ , is likely to be used to correlate the composition dependence of diffusion coefficients, activity coefficients, and the conductivity of the solution phase.

The specific interfacial area  $a$  is the surface area of the pore walls per unit volume of the total electrode. Let  $j_{in}$  be the pore-wall flux of species  $i$  averaged over this same interfacial area. The pore-wall flux to be averaged is the normal component of the flux of species  $i$  at the pore wall, relative to the velocity of the pore wall, and in the direction pointing into the solution. The pore wall may be moving slightly because of a dissolution process. Thus,  $aj_{in}$  represents the rate of transfer of the species from the solid phases to the pore solution (per unit volume of the total electrode).

Next, let  $N_i$  be the average flux of species  $i$  in the pore solution when averaged over the cross-sectional area of the electrode. Thus, for a plane surface, of normal unit vector  $\mathbf{n}$ , cutting the porous solid,  $\mathbf{n} \cdot N_i$  represents the amount of species  $i$  crossing this plane in the solution phase, but referred to the projected area of the whole plane rather than to the area of an individual phase.

The superficial current density  $i_2$  in the pore phase is due to the movement of charged solutes:

$$i_2 = F \sum_i z_i N_i \quad (1)$$

Similarly, the current density  $i_1$  in the matrix phase is defined to refer to the superficial area and not to the area of an individual phase.

## Material Balance for Solutes

Within a pore, in the absence of homogeneous chemical reactions, a differential material balance can be written for a species  $i$ . This equation can be integrated over the volume of the pores in an element of the electrode, and surface integrals can be introduced by means of the divergence theorem. Careful use of the definitions of average quantities yields (Dunning, 1971) the material balance for species  $i$ :

$$\frac{\partial \epsilon c_i}{\partial t} = a j_{in} - \nabla \cdot N_i \quad (2)$$

This result applies to the solvent as well as the solutes.

Three different averages are represented in Equation (2).  $c_i$  is an average over the volume of the solution in the pores.  $j_{in}$  is an average over the interfacial area between the matrix and the pore solution, and  $N_i$  is an average over a cross section through the electrode, cutting matrix and pore. Here, it should be borne in mind that the averages involve a volume which is large compared to the pore structure and small compared to the regions over which considerable macroscopic variations occur.

Equation (2) states that the concentration can change at a point within the porous electrode because the species moves away from the point (divergence of the flux  $N_i$ ) or because the species is involved in electrode processes (faradaic electrochemical reactions or double-layer charging) or simple dissolution of a solid material. This latter term  $a j_{in}$  resembles the term which would describe the bulk production of a species by homogeneous chemical reactions. In the macroscopic model, the transfer or creation from the matrix phases appears to occur throughout the bulk of the electrode because of the averaging process.

#### Electroneutrality and Conservation of Charge

A volume element within the porous electrode will be, in essence, electrically neutral because it requires a large electric force to create an appreciable separation of charge over an appreciable distance. We shall also take each phase separately to be electrically neutral. For the solution phase, this takes the form

$$\sum_i z_i c_i = 0 \quad (3)$$

Our assumption here means that the interfacial region which comprises the electric double layer (where departures from electroneutrality are significant) constitutes only a small volume compared to any of the phases or the electrode itself. This will not be true for finely porous media and very dilute solutions, where the diffuse layer may be more than 100 angstroms thick. Furthermore, we make no attempt here to treat electrokinetic effects like electro-osmosis and the streaming potential.

It is a consequence of the assumption of electroneutrality that the divergence of the total current density is zero. For the macroscopic model, this is expressed as

$$\nabla \cdot i_1 + \nabla \cdot i_2 = 0 \quad (4)$$

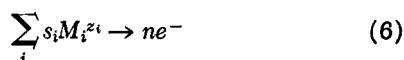
Charge which leaves the matrix phases must enter the pore solution. In fact, combination of Equations (1), (2), and (3) gives

$$\nabla \cdot i_2 = aF \sum_i z_i j_{in} = a i_n \quad (5)$$

where  $i_n$  is the average transfer current density (from the matrix phase to the solution phase).  $\nabla \cdot i_2$  is the transfer current per unit volume of the electrode ( $A/cm^3$ ) and has the direction of an anodic current.

#### Electrode Processes

For a single electrode reaction, represented as



Faraday's law is expressed as

$$a j_{in} = - \frac{a s_i}{nF} i_n = - \frac{s_i}{nF} \nabla \cdot i_2 \quad (7)$$

if the electrode is operating in a steady state or a pseudo steady state where double-layer charging can be ignored. Equation (2) becomes

$$\frac{\partial \epsilon c_i}{\partial t} = - \nabla \cdot N_i - \frac{s_i}{nF} \nabla \cdot i_2 \quad (8)$$

The polarization equation is necessary to express the dependence of the local rate of reaction on the various concentrations and on the potential jump at the matrix-solution interface. Electrode kinetics do not follow fundamental laws which can be written down as reliably as the law of conservation of matter. The situation is the same here as in chemical kinetics or heterogeneous catalysis. The polarization equation is the principal point where the macroscopic theory of porous electrodes will be subject to further refinement, as one tries to account not only for the mechanism of the charge-transfer process but also for the morphology of the electrode, the formation of covering layers or of crystallites of sparingly soluble species, and the transport from such sparingly soluble phases to the site of the charge-transfer process.

It is common to begin with a polarization equation of the form

$$\nabla \cdot i_2 = a i_0 \left[ \exp \left( \frac{\alpha_a F}{RT} \eta_s \right) - \exp \left( \frac{-\alpha_c F}{RT} \eta_s \right) \right] \quad (9)$$

where  $i_0$  is the exchange current density and  $\eta_s$  is the local value of the surface overpotential. The surface overpotential is the potential difference between the electrode and a (perhaps imaginary) reference electrode of the same kind as the working electrode and positioned adjacent to it, just beyond the double layer. The potential difference  $\Phi_1 - \Phi_2$  is equal to  $\eta_s$ , plus an additive term which depends on the local solution composition.

Consider a redox reaction like the oxidation of ferrous ions to ferric ions, thereby leaving the electrode structure unchanged. One frequently assumes that the composition dependence of the exchange current density and the composition dependence of the equilibrium potential cancel in such a way that the polarization equation can be written (see, for example, Newman, 1973, p. 388)

$$\nabla \cdot i_2 = a i_0 \left\{ \frac{c_1}{c_1^0} \exp \left[ \frac{\alpha_a F}{RT} (\Phi_1 - \Phi_2) \right] - \frac{c_2}{c_2^0} \exp \left[ \frac{-\alpha_c F}{RT} (\Phi_1 - \Phi_2) \right] \right\} \quad (10)$$

where  $i_0$  is a constant representing the exchange current density at the composition  $c_1^0$ ,  $c_2^0$ , which might conveniently be taken to be the initial concentrations of the reactants or the concentrations prevailing external to the electrode.

In Equation (10), the reaction is first order with respect to the reactant and product, at a given electrode potential. This would be obscured in Equation (9) because of the shift of the equilibrium potential with concentration, and  $i_0$  consequently has a fractional-power dependence on concentrations.

For a single electrode reaction, a material balance on the solid phases shows how the porosity changes with the extent of reaction at each location within the electrode:

$$\frac{\partial \epsilon}{\partial t} = - A_0 \nabla \cdot i_2 \quad (11)$$

where

$$A_0 = - \sum_{\text{solid phases}} \frac{s_i M_i}{\rho_i nF} \quad (12)$$

$M_i$  being the molecular weight and  $\rho_i$  the density of the solid phase (taken here to be a pure substance).

In addition to faradaic reactions, electrode processes can involve charging of the electric double layer at the interface between the pore solution and the conducting phases of the matrix. Let us, for the moment, exclude faradaic reactions and consider an ideally polarizable electrode—one which passes no steady current when held at a constant potential (within a certain range of allowed potentials).

For dependent variables we may choose  $q$ , the surface charge density on the electrode side of the double layer, and  $\Gamma_i$ , the surface excess or surface concentration of a solute species  $i$ . Here, we mean averages over the surface of the pores. These surface quantities can be taken to depend on the solution-phase composition, as represented by  $c_i$ , and on the electrode potential  $\Phi_1 - \Phi_2$ , where  $\Phi_2$  is measured with a given reference electrode. The relationship holds

$$q = -F \sum_i z_i \Gamma_i \quad (13)$$

since the interface as a whole is electrically neutral and the charge on the solution side of the double layer is comprised of the contributions of adsorbed solute species. For a solid surface it is only changes in  $q$  and  $\Gamma_i$  which can be determined easily and which are involved in impedance measurements and changes in solution composition. For a porous material of large specific area, one can, however, grind up the electrode and determine the magnitude of  $\Gamma_i$  by chemical analysis.

In the absence of electrokinetic effects, that is, ignoring translation of the solution side of the double layer in a direction parallel to the surface, one can express the material balance for a solute species at the interface as (Newman, 1973, p. 206)

$$\frac{\partial a \Gamma_i}{\partial t} = a j_{in, \text{faradaic}} - a j_{in} = -\frac{a s_i}{nF} i_{n, \text{faradaic}} - a j_{in} \quad (14)$$

where the subscript *faradaic* refers to charge or mass which is actually transported through the interface or is involved in a charge transfer reaction. It is assumed in the last form that only a single electrode reaction is involved. For the ideally polarizable electrode, these faradaic terms are taken to be zero. For a single electrode reaction, the left side of Equation (9) or (10) represents  $a i_{n, \text{faradaic}}$ .

Addition of Equation (14) according to Equation (5) gives

$$\nabla \cdot i_2 = a i_{n, \text{faradaic}} + \frac{\partial a q}{\partial t} \quad (15)$$

The current transferred from the matrix to the solution is involved either in double-layer charging or in faradaic electrode reactions.

The differential of the surface concentration can be expressed as

$$d\Gamma_i = \left( \frac{\partial \Gamma_i}{\partial U'} \right)_{c_j} dU' + \sum_{\substack{k \neq 0 \\ j \neq 0, k}} \left( \frac{\partial \Gamma_i}{\partial c_k} \right)_{U', c_j} dc_k \quad (16)$$

where  $U' = \Phi_1 - \Phi_2$ . This formidable equation indicates all the differential coefficients which must be known for an exact treatment of transient processes involving double-layer charging. These differential coefficients have been determined carefully for ideally polarizable mercury surfaces in relatively simple electrolytic solutions. Their estimation becomes inherently more difficult for solid surfaces, particularly in the presence of faradaic reactions. Nişan-

cioğlu (1973) and Appel (1974) have concerned themselves with this problem. Parsons (1970) has summarized earlier efforts and the relevant experimental data.

The differential double-layer capacity

$$C = \left( \frac{\partial q}{\partial U'} \right)_{c_j} = -F \sum_i z_i \left( \frac{\partial \Gamma_i}{\partial U'} \right)_{c_j} \quad (17)$$

is relatively easy to measure, and data are available over a wider range of concentrations.

In the absence of transient concentration variations, and with a constant specific interfacial area, Equation (15) reduces to

$$\nabla \cdot i_2 = a f(U', c_i) + a C \frac{\partial U'}{\partial t} \quad (18)$$

an equation which can be used to analyze double-layer charging in porous electrodes.

Analysis of electrode processes is the basis for evaluating the term  $a j_{in}$  in the material balance Equation (2). The general case involving double-layer charging and all the differential coefficients in Equation (16) becomes too complicated to pursue profitably at this point.

#### Transport Processes

In the matrix phase, the movement of electrons is governed by Ohm's law

$$i_1 = -\sigma \nabla \Phi_1 \quad (19)$$

where  $\sigma$  is the effective conductivity of the matrix. This quantity will be affected by the volume fraction of the conducting phase or phases, the inherent conductivity of each conducting solid phase, and the manner in which granules of conducting phases are connected together.

In a dilute electrolytic solution within the pores, the flux of mobile solutes can be attributed to diffusion, dispersion, migration, and convection:

$$\frac{N_i}{\epsilon} = -(D_i + D_a) \nabla c_i - z_i u_i F c_i \nabla \Phi_2 + \frac{v c_i}{\epsilon} \quad (20)$$

Since  $N_i$  is the superficial flux based on the area of both matrix and pore, one can think of  $N_i/\epsilon$  as the flux in the solution phase. Similarly,  $v/\epsilon$  will be roughly the velocity in the solution phase if we take  $v$  to be a superficial bulk fluid velocity, for example, the volumetric flow rate entering the electrode divided by its superficial area. The molar-average velocity  $v^*$  would thus be given by

$$c_T v^* = \sum_i N_i \quad (21)$$

where

$$c_T = \sum_i c_i \quad (22)$$

is the total solution concentration. (The solvent is to be included in both these sums.)

The ionic diffusion coefficient and mobility of a free solution require a correction for the tortuosity of the pores in order to yield  $D_i$  and  $u_i$ . A porosity factor has already been taken out; that is,  $\epsilon D_i$  might logically be regarded to be the effective diffusion coefficient of the species in the pore solution in the same way that  $\sigma$  is the effective conductivity of the matrix. Estimation of such physical properties is considered again in a later section.

$D_a$  represents the effect of axial dispersion—the attenuation of concentration gradients as a fluid flows through a porous medium. Plug flow does not prevail in the pores; fluid near the wall moves more slowly than fluid toward the center of the void space. The compensation for this convective nonideality appears as a diffusion phenomenon.

However, the dispersion coefficient is not a fundamental transport property—it depends on the fluid mixing and vanishes in the absence of convective fluid motion. A correlation is given in the section on flow-through porous electrodes. Dispersion should properly be represented by a tensor coefficient since dispersion is different in directions parallel to and perpendicular to the bulk flow velocity  $\mathbf{v}$ .

The current density in the solution phase according to Equation (1) now becomes

$$i_2 = -\kappa \nabla \Phi_2 - \epsilon F \sum_i z_i D_i \nabla c_i \quad (23)$$

where

$$\kappa = \epsilon F^2 \sum_i z_i^2 u_i c_i \quad (24)$$

is the effective conductivity of the solution phase. The second term on the right in Equation (23) represents the diffusion potential. Convection and dispersion have made no contribution in this equation since the solution is electrically neutral. If the ionic diffusion coefficients are all equal, the diffusion-potential term will disappear as well.

There are two limiting cases which are likely to receive treatment. For the reaction of a minor component from a solution with excess supporting electrolyte, migration is neglected. Equations (20) and (2) become

$$\frac{\partial \epsilon c_i}{\partial t} + \nabla \cdot [v c_i] = a j_{in} + \nabla \cdot [(D_i + D_a) \epsilon \nabla c_i] \quad (25)$$

For assessing the potential variation within the solution, one is tempted to neglect the diffusion potential in Equation (23) and take the conductivity  $\kappa$  to be constant (for uniform porosity). However, on the basis of a small ratio of reactant to supporting electrolyte, one is occasionally justified in neglecting the potential variation altogether.

The binary electrolyte, the other limiting case, is simple because only two ionic species are present. The electroneutrality condition (3) then allows the electrolyte concentration to be defined as

$$c = c_+ / \nu_+ = c_- / \nu_- \quad (26)$$

Space will not be devoted to dilute-solution theory for this situation since it is mainly of interest in comparison with the more complete treatment in the next subsection.

### Concentrated Binary Electrolyte

Many battery systems involve solutions of a single electrolyte. Consequently, it is desirable to develop the theory with all possible exactness, particularly since the equations to use are not hopelessly complicated and thermodynamic and transport data are frequently available for binary solutions. Newman et al. (1965) developed the transport equations in terms of the molar-average velocity. Newman (1967) states the results with the mass-average velocity and the solvent velocity, while Newman and Chapman (1973) showed how the volume-average velocity can be used.

The superficial volume-average velocity  $\mathbf{v}^\square$  is defined as

$$\mathbf{v}^\square = \bar{V}_0 \mathbf{N}_0 + \bar{V}_+ \mathbf{N}_+ + \bar{V}_- \mathbf{N}_- \quad (27)$$

where  $\bar{V}_+$  and  $\bar{V}_-$  satisfy

$$\nu_+ \bar{V}_+ + \nu_- \bar{V}_- = \bar{V}_e \quad (28)$$

This is not sufficient to determine the partial molar volumes of the ions separately. Consequently, we let

$$\nu_+ \bar{V}_+ = t_-^0 \bar{V}_e \quad \text{or} \quad t_+^0 \nu_+ \bar{V}_+ = t_-^0 \nu_- \bar{V}_- \quad (29)$$

In other words, the transference numbers of the ions are assumed to be inversely proportional to their partial molar volumes. However, this choice is based solely on convenience (Newman and Chapman, 1973), and no physical significance should be attached to it.

The cation flux can now be expressed as

$$\mathbf{N}_+ = c_+ \mathbf{v}^\square - \epsilon (D + D_a) \nabla c_+ + \frac{t_+^0}{z_+ F} i_2 \quad (30)$$

with a similar expression for the anion flux, and the solvent flux is

$$\mathbf{N}_0 = c_0 \mathbf{v}^\square - \epsilon (D + D_a) \nabla c_0 \quad (31)$$

Here  $D$  is the effective diffusion coefficient of the electrolyte.

Substitution of these fluxes into the material balance 2 and rearrangement gives two fundamental equations for porous electrodes involving a binary electrolyte:

$$\begin{aligned} \frac{\partial \epsilon}{\partial t} + \nabla \cdot \mathbf{v}^\square = a \left[ \bar{V}_0 j_{0n} + \frac{\bar{V}_e t_-^0}{\nu_+} j_{+n} + \frac{\bar{V}_e t_+^0}{\nu_-} j_{-n} \right] \\ - \bar{V}_e \frac{i_2 \cdot \nabla t_+^0}{z_+ \nu_+ F} - \epsilon \frac{D + D_a}{c_0 \bar{V}_0} (\nabla c) \cdot \nabla \bar{V}_e \end{aligned} \quad (32)$$

and

$$\begin{aligned} \epsilon \frac{\partial c}{\partial t} + \mathbf{v}^\square \cdot \nabla c = \nabla \cdot [\epsilon (D + D_a) \nabla c] \\ - c_0 \bar{V}_0 \frac{i_2 \cdot \nabla t_+^0}{z_+ \nu_+ F} + a c_0 \bar{V}_0 \left( \frac{t_-^0}{\nu_+} j_{+n} + \frac{t_+^0}{\nu_-} j_{-n} \right) \\ - a c \bar{V}_0 j_{0n} + \frac{c \epsilon (D + D_a)}{c_0 \bar{V}_0} (\nabla c) \cdot \nabla \bar{V}_e \end{aligned} \quad (33)$$

Equation (32) is an overall conservation equation, expressing perhaps conservation of volume. It shows how the velocity  $\mathbf{v}^\square$  changes as a result of an electrode reaction and the changing composition of the solution.

Equation (33) is a material balance for the electrolyte. The corresponding equation in the dilute-solution approximation does not reflect the dilution which would occur if the solvent were to be produced in an electrode reaction. The equations become quite similar if one is willing to neglect the concentration dependence of both the partial molar volume  $\bar{V}_e$  of the electrolyte and the cation transference number  $t_+^0$  with respect to the solvent velocity.

Instead of Equation (23), we may wish to express Ohm's law in the form (see Newman, 1973, Equation 81-8)

$$\frac{i_2}{\kappa} = -\nabla \Phi_2 - \left( \frac{s_+}{\nu_+ n} + \frac{t_+^0}{z_+ \nu_+} - \frac{s_0 c}{n c_0} \right) \frac{\nabla \mu_e}{F} \quad (34)$$

where  $\Phi_2$  is the potential in the pore solution measured with a reference electrode having the stoichiometric coefficients  $s_i$  and number  $n$  of electrons transferred, and  $\mu_e$  is the chemical potential of the electrolyte.

### Summary

The structure of equations describing the porous electrode does have order. A certain level of complication is necessary in order to treat the physical processes which are involved. Equation (19) covers transport in the matrix, while Equations (1), (2), (3), and (20) relate to transport, conservation, and electroneutrality in the solution phase. However, the bulk appearance of a species is now related to electrode processes occurring throughout the volume. Thus, Equations (4) and (9), representing boundary conditions between the phases, must apply here throughout the volume.

Complications and uncertainties are largely related to

electrode processes. Changes in the structure and properties of the electrode need to be related to the local extent of discharge or the integral of the local transfer current  $\nabla \cdot i_2$ .

### NONUNIFORM REACTION RATES

Many special cases are treated in the literature. The simplest assume that the solution phase is uniform in composition—either because the current has just been switched on and the concentrations have not had time to change or because there is forced convection through the electrode so as to maintain the composition uniform. Double-layer charging is also to be ignored. Still open to the investigator's choice are the relative electric conductivities of the two phases, the thickness of the electrode, and the form of the polarization equation expressing the electrochemical kinetics.

Consider a porous electrode in the form of a slab of thickness  $L$ . The electrode is in contact with an equipotential metal surface on one side at  $x = L$  and in contact with an electrolytic solution on the other at  $x = 0$ . In such problems it is convenient to specify the superficial current density  $I$  flowing through the electrode rather than the potential difference across it. Positive values of  $I$  will correspond to anodic currents. The structure of the electrode will be taken to be uniform.

The four governing differential equations take on a one-dimensional form. Equation (4) expresses conservation of charge, Equation (23) reduces to Ohm's law for the pore solution, and Equation (19) is the same law for the matrix. The polarization Equation (9), with  $\eta_s = \Phi_1 - \Phi_2$ , describes the transfer of charge from the matrix to the solution. Sufficient boundary conditions include

$$i_2 = -I, \quad i_1 = 0, \quad \text{and} \quad \Phi_2 = 0 \quad \text{at} \quad x = 0 \quad (35)$$

$$i_2 = 0 \quad \text{at} \quad x = L \quad (36)$$

These say that at the electrode-solution interface ( $x = 0$ ) the current is carried entirely by the pore electrolyte while at the metal backing, the current is carried entirely by the matrix. As an arbitrary reference of potential, we choose  $\Phi_2 = 0$  at  $x = 0$ . Somewhere within the electrode, between  $x = 0$  and  $x = L$ , the current is transferred from the solution to the matrix, and the rate of reaction is proportional to  $di_2/dx$ .

The reaction distribution is generally nonuniform within the electrode. To minimize the ohmic potential drop, the current should be divided between the solution and the matrix in proportion to their effective conductivities. However, this requires high reaction rates near  $x = 0$  and  $x = L$ . Slow electrode reaction kinetics force the reaction to be more uniformly distributed in order to reduce the transfer current density. These competing effects of ohmic potential drop and slow reaction kinetics determine the resulting distribution.

For the problem as formulated above, four dimensionless ratios govern the current distribution. These can be stated as a dimensionless current density

$$\delta = \frac{\alpha_a F I L}{RT} \left( \frac{1}{\kappa} + \frac{1}{\sigma} \right) \quad (37)$$

a dimensionless exchange current for the electrode

$$\nu^2 = (\alpha_a + \alpha_c) \frac{F a i_0 L^2}{RT} \left( \frac{1}{\kappa} + \frac{1}{\sigma} \right) \quad (38)$$

the ratio  $\alpha_a/\alpha_c$  of the transfer coefficients in the polarization Equation (9), and the ratio  $\kappa/\sigma$  of the effective conductivities of the solution and matrix phases.

The first two,  $\delta$  and  $\nu^2$ , are ratios of the competing effects of ohmic potential drop and slow electrode kinetics. For

large values of either  $\delta$  or  $\nu^2$ , the ohmic effect dominates, and the reaction distribution is nonuniform. The ratio  $\alpha_a/\alpha_c$  seems to be unavoidable, but its role is more difficult to discern. For small values of  $\kappa/\sigma$ , the reaction occurs preferentially near the electrode-solution boundary at the expense of the region near the backing plate.

The description of a porous electrode in the absence of concentration variations is similar to that of the secondary current distribution at a disk electrode (Newman, 1973, section 117). It is customary to introduce one of two approximations to the polarization Equation (9). For very low overpotentials, this equation can be linearized to read

$$\frac{di_2}{dx} = (\alpha_a + \alpha_c) \frac{a i_0 F}{RT} (\Phi_1 - \Phi_2) \quad (39)$$

On the other hand, at very high overpotentials, one or the other of the terms on the right in Equation (9) can be neglected. The first term is neglected for a cathode; the last term for an anode. This is referred to as the *Tafel approximation*.

For systems with a finite conductivity of each phase, the solution of these equations with the linear electrode kinetics has been given by Euler and Nonnenmacher (1960) and restated by Newman and Tobias (1962). These last workers also obtained the solution for Tafel polarization, while Micka (1965) was able to treat the complete Equation (9) in the special case where  $\alpha_a = \alpha_c$ . Daniel-Bek (1948) had earlier presented the results for linear and Tafel kinetics in the case where the current collector is positioned at the electrode-solution boundary instead of being at  $x = L$ .

Many papers deal with matrix conductivities much greater than the solution conductivity, so that the matrix potential  $\Phi_1$  is uniform. It then becomes possible to treat very thick electrodes, where the analysis is similar to that for the diffuse part of the electric double layer (Newman, 1973, section 52), as pointed out by Frumkin (1949). Frumkin gave solutions for linear kinetics [Equation (39)] and also for the full Equation (9) for the special case where  $\alpha_a = \alpha_c$ . He spoke, however, in terms of corrosion processes in the interior of a tube. Ksenzhek and Stender (1956b) gave the solution in the context of porous electrodes. For semi-infinite electrodes, Posey (1964) extended this work to the cases  $\alpha_a = 2\alpha_c$  and  $3\alpha_c$  (as well as the reciprocal cases where  $\alpha_c$  equals  $2\alpha_a$  or  $3\alpha_a$ ). For semi-infinite electrodes, the gross current-potential behavior can be obtained immediately for any ratio of  $\alpha_a$  to  $\alpha_c$ , by analogy with the theory for the diffuse part of the electric double layer. Then

$$I^2 = \frac{2a i_0 \kappa RT}{\alpha_a \alpha_c F} \left[ \alpha_c \exp \left( \frac{\alpha_a F V}{RT} \right) + \alpha_a \exp \left( - \frac{\alpha_c F V}{RT} \right) - \alpha_a - \alpha_c \right] \quad (40)$$

where  $V = \Phi_1 - \Phi_2$  at  $x = 0$ , the solution side of the electrode.

For finite electrodes and a high matrix conductivity, Ksenzhek (1962b) and Winsel (1962) give solutions for  $\alpha_a = \alpha_c$  in Equation (9). Posey (1964) was able to include the case  $\alpha_a = 2\alpha_c$  (or the converse,  $\alpha_c = 2\alpha_a$ ). He also gives approximate solutions for all values of  $\alpha_a/\alpha_c$ .

One feature of the results is the nonuniformity of the reaction rate within the electrode. Figure 1 shows the distribution of reaction rate for Tafel kinetics and for  $\sigma = \kappa$ . As in the classical secondary-current-distribution problem, the value of  $a i_0$  is unimportant as long as the backward reaction can truly be neglected. In the Tafel case, the current distribution depends only on the parameter  $\delta$  and on

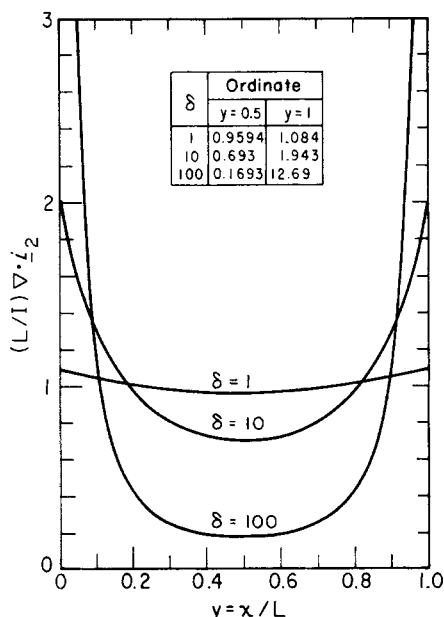


Fig. 1. Reduced current distributions for Tafel polarization with  $\sigma = \kappa$ .

the ratio  $\kappa/\sigma$ . (For cathodic polarization in the Tafel range, replace  $\alpha_a$  by  $-\alpha_c$  in Equation (37) in order to use these results.) For a small value of  $\delta$ , the reaction is uniform; but for large values of  $\delta$ , the reaction takes place mainly at the electrode interfaces. The ratio  $\kappa/\sigma$  serves to shift the reaction from one face to the other so that the reaction is somewhat more uniform as  $\kappa$  approaches  $\sigma$  at constant  $\delta$ .

Curves for the linear-polarization equation would have the same general appearance as Figure 1. In analogy with the classical problem of the secondary current distribution, the reduced distribution depends only on the parameter  $\nu$  and on the ratio  $\kappa/\sigma$  and is independent of the magnitude of the current. The distribution becomes non-uniform for large values of  $\nu$ , that is, for large values of the exchange current density, the specific interfacial area, or the electrode thickness or for small values of the conductivities. The ratio  $\kappa/\sigma$  still shifts the reaction from one face to the other.

The distance to which the reaction can penetrate the electrode determines how thick an electrode can be effectively utilized. This penetration depth is characterized by the length

$$\frac{L}{\nu} = \sqrt{\frac{RT\kappa\sigma}{(\alpha_a + \alpha_c)ai_0F(\kappa + \sigma)}} \quad (41)$$

Frumkin (1949) pointed out the analogy of the penetration depth to the Debye length in diffuse-double-layer theory. The concept of the penetration depth has also been emphasized by Ksenzhek and Stender (1956b) and by Winsel (1962). Electrodes much thinner than the penetration depth behave like plane electrodes with an enhanced surface area. Electrodes much thicker are not fully utilized. At high current levels,  $L/\delta$  is a length which may be more characteristic of the penetration of the reaction. For diffusive transport of reactants or consumption of reactants stored in the matrix or the pore solution, other factors will enter into the optimization of the electrode thickness.

Potential distributions for Tafel kinetics are illustrated in Figure 2 for

$$\alpha_a \frac{Fai_0L^2}{RT} \left( \frac{1}{\kappa} + \frac{1}{\sigma} \right) = 0.1 \quad (42)$$

(For Tafel kinetics, with a given value of  $I$ , changes in  $ai_0$  merely add a constant to  $\Phi_1 - \Phi_2$  without affecting the current or potential distributions in any other way.) The slope of the curves gives the current density flowing in either the matrix or the pore solution, according to Ohm's law. Consequently, the second derivative of either  $\Phi_1$  or  $\Phi_2$  is related to the local reaction rate or the rate at which current is transferred from one phase to the other. The difference  $\Phi_1 - \Phi_2$  also gives this reaction rate through the polarization equation.

The total potential loss in the electrode, a combination of kinetic or surface overpotential and ohmic potential drop, is given by the difference between the potential  $\Phi_1$  in the matrix at the current collector and the potential  $\Phi_2$  in the pore solution at the pore mouth [where  $\Phi_2$  was actually taken to be zero in Equation (35)]. For linear polarization, this loss can be expressed as

$$\frac{\Phi_1(L) - \Phi_2(0)}{I} = \frac{L}{\kappa + \sigma} \left[ 1 + \frac{2 + \left( \frac{\sigma}{\kappa} + \frac{\kappa}{\sigma} \right) \cosh \nu}{\nu \sinh \nu} \right] \quad (43)$$

The potential loss for Tafel polarization is plotted in Figure 3 under the condition of Equation (42). This corresponds to the so-called "Tafel plot" and has a slope of 2.303 for low values of  $\delta$ . As  $\delta$  increases, the potential drop due to resistance becomes important. For a high conductivity of one phase, a double Tafel slope results, as pointed out by Ksenzhek and Stender (1956b) and by Winsel (1962), among others. Thus, the lower curve in Figure 3 attains a slope of 4.605 for large  $\delta$ . If both conductivities are finite, the ohmic contribution to the potential loss will eventually dominate. Thus, the upper curve in Figure 3 becomes linear in  $\delta$ , not linear in the logarithm of  $\delta$ . The behavior of both curves for large  $\delta$  illustrates the general rule that the ohmic potential drop becomes more important at large currents.

The Tafel approximation becomes poor at low currents. One cannot extrapolate Figure 3 since  $\beta\Phi_1(L)$  should approach zero as  $\delta$  approaches zero. The backward reaction

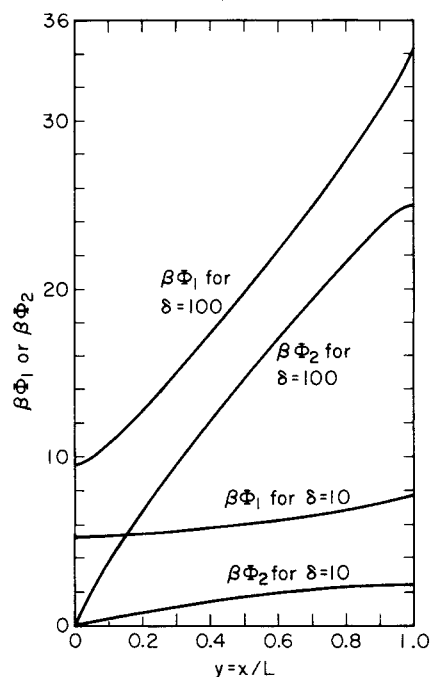


Fig. 2. Potential distributions for Tafel polarization with  $\sigma = \kappa$ . Here  $\beta = \alpha_a F/RT$  (or  $-\alpha_c F/RT$  for cathodic currents).

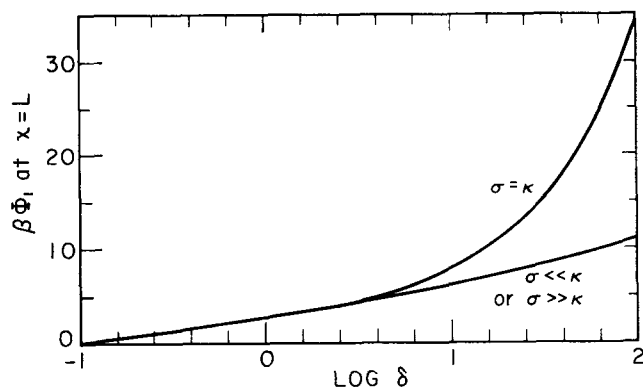


Fig. 3. Potential of the metal backing plate as it depends on  $\delta$ . Here  $\beta = \alpha_a F/RT$  (or  $-\alpha_c F/RT$  for cathodic currents).

should be accounted for, and eventually the linear approximation becomes applicable at very low values of  $\delta$ . Equation (40) gives the current-potential relation for a semi-infinite electrode with a high conductivity of one phase, and Equation (43) is the result without these restrictions but instead restricted to the linear approximation.

## MASS TRANSFER

### Steady Mass Transfer

A solution-phase reactant is depleted during the operation of a porous electrode, and diffusion of this species from a reservoir at the face of the electrode represents a loss, in addition to the ohmic potential drop and surface overpotential considered in the previous section.

Two special problems might be defined in this area. The first involves a redox reaction obeying Equation (10). The reactant and product species, whose stoichiometric coefficients are taken to be +1 and -1, move by molecular diffusion alone since convection is assumed to be absent and migration is negligible because an excess of supporting electrolyte is presumed to be present. This excess of supporting electrolyte is also used to justify the approximation of a constant solution-phase conductivity  $\kappa$  and neglect of the diffusion potential\* so that Equation (23) reduces to Ohm's law for the solution phase. The second special case involves a binary electrolyte, where the solution-phase conductivity can be taken to be proportional to the concentration.

The first special case was treated by Newman and Tobias [1962, with neglect of the reverse reaction in Equation (10)], by Ksenzhek (1962a, also for an infinitely thick electrode and with negligible ohmic potential drop in either phase), and by Gurevich and Bagotskii (1963a, b, summarized and more readily accessible in 1964). For each species, two new parameters are introduced—a diffusion coefficient and a bulk or characteristic concentration  $c_i^0$ . These can be combined into the dimensionless group  $\gamma_i = s_i l L / n F \epsilon D_i c_i^0$ .

With negligible ohmic potential drop in either phase, the reaction rate distribution is given by

\* In the steady state, the diffusion potential can be included, without a separate term, by using a modified conductivity:

$$\kappa' = -n\epsilon F^2 \frac{\sum_i z_i^2 u_i c_i / D_i}{\sum_i z_i s_i / D_i}$$

$$\nabla \cdot i_2 = a i_0 \frac{\cosh k_1(L-x)}{\cosh k_1 L} \left[ \exp\left(\frac{\alpha_a F V}{RT}\right) - \exp\left(-\frac{\alpha_c F V}{RT}\right) \right] \quad (44)$$

and the current-potential relation is given by

$$I = \frac{a i_0}{k_1} \tanh k_1 L \left[ \exp\left(\frac{\alpha_a F V}{RT}\right) - \exp\left(-\frac{\alpha_c F V}{RT}\right) \right] \quad (45)$$

where

$$k_1^2 = \frac{a i_0}{\epsilon F D_1 c_1^0} \left[ \exp\left(\frac{\alpha_a F V}{RT}\right) + \frac{D_1 c_1^0}{D_2 c_2^0} \exp\left(-\frac{\alpha_c F V}{RT}\right) \right] \quad (46)$$

Mass transfer limitations external to the electrode should also be included. We have taken  $c_i^0$  to be the concentration at the face of the electrode, adjacent to the solution.

The penetration depth can be taken to be the reciprocal of  $k_1$  (compare Ksenzhek, 1962a), and for large anodic polarization this becomes equal to  $L/\gamma_1$ . Equations (45) and (46) also give a double Tafel slope at high polarization. This phenomenon, due to a mass-transfer effect, has been pointed out by Ksenzhek (1962a), by Gurevich and Bagotskii (1963b), and by Austin and Lerner (1964) and has been contrasted with the double Tafel slope, mentioned below Equation (43), due to an ohmic effect. Austin (1964) has examined the relative importance of these two effects on the basis of the ratio  $\alpha_a n F^2 \epsilon D_1 c_1^0 / s_1 R T \kappa \approx \delta/\gamma_1$ .

Gurevich and Bagotskii have developed complicated analytic solutions for the first special case. These become so complicated that limiting cases (discussed above) must be examined or machine computation becomes convenient. Bomben (1963) presents computer programs for this case and also the situation where the reverse reaction term in Equation (10) can be neglected. Grens and Tobias (1965), using a computer program which includes mass transfer of each species, including the supporting electrolyte, have made comparisons with analytic solutions concerning variations of composition and conductivity and approximations to the polarization equation. In this manner, Grens (1970) has examined assumptions of the one-dimensional approximation (see also de Levie, 1967), of infinitely thick electrodes, of uniform concentration or conductivity, and of negligible potential gradient in the pores. Today, one could also test (or relax) the assumptions of invariant electrode matrix, constant diffusion coefficients and mobilities, and absence of fluid flow, even that due to the reaction itself. Austin (1969) has reasserted the value of analytic solutions for limiting situations.

Deposition from a binary electrolyte has been treated by Newman and Tobias (1962) and by Micka (1966). Bomben (1963) gives a computer program suitable for the Tafel case.

Posey and Misra (1966) and later Alkire (1973) have treated, by computer simulation, bipolar porous electrodes, that is, electrodes with no external electrical connection but with induced polarization because a current passes through them. The apparent resistance of the porous electrode is different from that of an equal volume of solution not only because the porosity is less than one but also because the current has the possibility of reacting cathodically on one side of the electrode, flowing through the matrix, and emerging by anodic reaction at the other side of the electrode. With a bipolar tubular gold electrode, Posey and Misra were able to determine the transfer coefficient of the ferricyanide-ferrocyanide redox reaction.



## Transient Mass Transfer

To follow the course of the discharge of a porous electrode, beginning with a uniform solution composition and following the development toward a steady state, requires a consideration of the time derivative in Equation (8).

Stein (1959, see also Newman, 1962) treated the change of sulfuric acid concentration in the pores of a lead acid battery. The performance during a very high rate discharge is limited by a severe depletion of acid directly at the mouth of the pores of the positive plate. To study this effect, Stein was able to avoid consideration of structural changes, and he assumed that the electrode reaction itself occurred reversibly.

Grens and Tobias (1964) undertook a computer analysis including migration and diffusion of each solute species and a polarization equation like Equation (10). The cadmium anode in KOH and the reduction of ferricyanide in NaOH received detailed treatment.

A characteristic time for diffusion processes is  $L^2/D_i$ . For an electrode thickness of 0.1 cm and an effective diffusion coefficient of  $10^{-5}$  cm<sup>2</sup>/s, this leads to diffusion times of the order of 1000 s. However, for thick electrodes, the presence of a reservoir of unreacted species in the depth has little effect on the dominant processes occurring near the solution side of the electrode. The penetration depth [see, for example, Equation (46)] can then be used rather than  $L$  in forming the characteristic time for diffusion. Thus, 90% of the electrode potential change can occur in a time as short as 30 s. (The characteristic time for charging the double-layer capacity is usually much less. The ratio of the double-layer-charging time to the diffusion time is  $D_i C/\kappa$ . This ratio is greater than one only for very high interfacial areas and low conductivities.)

## BATTERY SIMULATION

Porous electrodes used in primary and secondary batteries invariably involve solid reactants and products, and the matrix is changed during discharge. Consequently, no steady state operation is strictly possible. Such systems are complex, and their simulation on the computer is an active area of research.

### Structural Changes

Winsel (1962) allowed for the consumption of a solid reactant by setting the transfer current equal to zero at any point in the electrode where the charge passed was equal to that which this fuel could supply. Because of the nonuniform current distribution, the solid fuel is exhausted first at the side of the electrode adjacent to the solution. Cutting off the reaction in this region forces a higher average reaction rate in the remainder of the porous structure (for a constant-current discharge), yielding a higher electrode overpotential. The ohmic potential drop in the solution in the depleted part of the electrode also contributes significantly to the overpotential. Winsel could thus describe battery discharge without accounting for the composition variation in the solution or changes in the matrix porosity.

Alkire et al. (1969b) treated the change in pore size and solution composition and the attendant fluid flow for dissolution of porous copper in sulfuric acid solution. The treatment of a straight-pore system is particularly appropriate here since they were able to wind copper wire carefully and sinter the coil to produce a uniform pore structure (Alkire et al., 1969a). In contrast to the work of Grens and Tobias (1964), the time derivative of solution concentration was neglected (resulting in a so-called "pseudo steady state analysis").

Dunning and Bennion (1969) developed a model for battery electrodes with a description of mass transfer from

nonconducting crystallites of sparingly soluble fuel to conducting particles which are the site of the electrochemical reaction. They obtained an analytic solution exhibiting a limiting current due to internal mass-transfer limitations, and they discussed acceptable limits of the solubility of the sparingly soluble reactant. Self discharge can impose an upper limit, and adequate power density, a lower limit. Later, Dunning et al. (1971) analyzed discharge and cycling, with the internal mass-transfer coefficient dependent on the local state of charge. The next work (Dunning et al., 1973) included discharge and cycling of silver-silver chloride and cadmium-cadmium hydroxide electrodes in binary electrolytes of NaCl and KOH, respectively. The mechanism of discharge included, in series, the kinetics of dissolution or precipitation of the sparingly soluble fuel, the diffusion to the reaction site, and the electrochemical kinetics of the reaction—with regard for the changes in the areas available for these processes. Also accounted for were porosity changes according to Equations (11) and (12), fluid flow according to Equation (32) (or its equivalent), variations in conductivity and activity coefficient in the use of Equation (34), and electrolyte transport according to Equation (33) (or its equivalent). However, the concentration derivative in this equation was neglected (pseudo steady state).

Alkire and Place (1972) have analyzed the consumption of a solid reactant as did Winsel (1962) but with treatment of the solution composition according to the pseudo steady state method. The calculations apply specifically to copper dissolution from an inert porous substrate, for example, stainless steel.

The lead dioxide electrode has been modeled recently by both Simonsson (1973b, c) and by Micka and Roušar (1973). The former analysis appears to be comprehensive; the latter follows Stein (1959) in assuming reversible electrode kinetics. This leads to the conclusion that the potential in the pore electrolyte is a unique function of the concentration, and this obscures the formulation of boundary conditions (Newman, 1962). In the two papers, the figures of concentration versus position within the electrode, with time as a parameter, provide an interesting contrast. Simonsson assumed a constant concentration at the pore mouth; Micka and Roušar show a concentration which eventually goes to zero at the pore mouth.

Gidaspow and Baker (1973) emphasize porosity changes and blocking of the pores as a mechanism of battery failure.

One now discerns a number of factors which can affect the extent of utilization of a battery as a function of rate of discharge:

1. Higher current densities yield higher overpotentials, and thus a given cutoff potential is reached sooner. However, this must be considered in conjunction with a factor which leads to a time dependence of the potential.
2. Acid depletion at the pore mouth (Stein, 1959) hastens the end of discharge of the lead acid battery, particularly at high current densities.
3. The pores may become constricted or even plugged with solid reaction products. A nonuniform reaction distribution will accentuate this problem at the mouth of the pores.
4. Utilization of the solid fuel and covering of the reaction surface with reaction products. Notice that both Dunning et al. (1973) and Simonsson (1973b) assumed that the local extent of utilization was constrained to be incomplete, and Simonsson allowed this limit to depend on the discharge current density.
5. Rates of mass transfer between crystallites and the reaction surface may become more limiting as the discharge exhausts the front part of the electrode. This could

account for changes in the apparent limit of utilization with current density.

### Optimization of Electrode Thickness

Advice on how thick to build a porous electrode (Ksenzhek, 1962b; Gurevich and Bagotskii, 1969) does not go significantly beyond pointing out that polarization decreases little for increasing thickness beyond the penetration depth [see Equations (41) and (46)], because of the poor utilization of the added material. We should expect, however, to find cost, weight, and volume optimization for given duty cycles and cut-off potentials.

### Machine Computation

The complexity of the factors which we wish to include in the analysis of the behavior of porous electrodes leads many of us to use a high-speed digital computer.

For battery electrodes involving a binary electrolyte, let us suggest the following computational scheme (Dunning, 1971). Equations (32) and (33) simplify considerably with assumptions of constant transference numbers and partial molar volumes. Equations (7), (11), and (32) can then be combined and integrated to relate the velocity to the current density

$$v = \left[ A_0 - \frac{V_{0s0}}{nF} - \frac{V_e}{nF} \left( \frac{t_{-0}s_+}{\nu_+} + \frac{t_{+0}s_-}{\nu_-} \right) \right] i_2 \quad (47)$$

with the boundary condition that both  $v$  and  $i_2$  vanish at a plane of symmetry or the backing plate.

For a highly conducting matrix ( $\sigma \gg \kappa$ ), one can use four principal unknowns—the electrolyte concentration  $c$ , the current density  $i_2$ , the transfer current  $j = \nabla \cdot i_2$ , and the solution potential  $\Phi_2$  (or, equivalently, the local electrode overpotential). The velocity is eliminated by means of Equation (47), and the porosity is related to the transfer current density and the time step by Equation (11).

We have then programmed four equations for simultaneous solution as coupled, ordinary, nonlinear, differential equations at each time step, with boundary conditions at two values of  $x$  (Newman, 1968, 1973-appendix C).

Straightforward to program are the relation  $j = \nabla \cdot i_2$  and Equation (34) representing Ohm's law. The activity coefficients (relating  $\mu_e$  to  $c$ ) and the conductivity can be taken to depend on the concentration. The porosity dependence of  $\kappa$  should be accounted for, and the equations must be linearized properly to assure convergence.

We have programmed Equation (33) symmetrically between the old time step and the present one, in order to attain stability. Simplifications were made for constant transference numbers and partial molar volumes, and  $D_a$  was set equal to zero. Both the porosity and concentration dependence of  $D$  were included. The pseudo steady state approximation results when the time derivative of concentration is omitted from this equation. Simonsson (1973c) finds that this approximation is valid for low discharge rates but can lead to appreciable error for rapid discharge.

Finally, the polarization equation relates the transfer current  $j$  to the concentration and overpotential. One can include here complexing and mass transfer of a sparingly soluble reactant and electrochemical kinetics on a surface area which changes with the local state of charge.

The boundary conditions can be made to include a limited reservoir of solution adjacent to the electrode and perhaps even a remote reservoir, connected to the adjacent reservoir by a mass-transfer coefficient. This will allow simulation of the recovery of the electrode potential with time as the electrolyte concentration is restored. A complete lead-acid cell can be simulated by juxtaposition (in the computer) of a porous lead electrode and a porous

lead dioxide electrode. Such electrodes or cells can be cycled with current (or potential) as an arbitrary function of time.

### DOUBLE-LAYER CHARGING AND ADSORPTION

A measurement of the double-layer capacity of a porous electrode most directly reflects the active surface area coherently connected electrically and therefore accessible for electrochemical reactions. Changes in the nature of the solid phase composition, surface crystal structure, adsorbed materials, solution composition, temperature, and electrode potential also influence the measured value. Such results should be useful for the characterization of battery electrodes and may be especially valuable since the electrode is not destroyed, and indeed need not be removed from the cell in which it is being studied.

There have been many contributions to the theoretical understanding of double-layer charging. Ksenzhek and Stender (1956a) were the first to treat the subject, and further refinements have included development of a macrohomogeneous model (Ksenzhek and Stender, 1956b; Newman and Tobias, 1962) and treatment of coupled faradaic reactions (Ksenzhek, 1963; Austin and Gagnon, 1973), changes in solution composition (Ksenzhek, 1964; Johnson and Newman, 1971), effects of external surface area (Ksenzhek, 1964; Posey and Morozumi, 1966) finite conductivity  $\sigma$  of the electrode matrix (Posey and Morozumi; Johnson and Newman), effect of ohmic potential drop external to the porous electrode (Posey and Morozumi; Johnson and Newman; Tiedemann and Newman, 1974), and imposed alternating current (Winsel, 1962; de Levie, 1963, 1967; Darby, 1966a, b).

Experimental verification of these models has been performed by Stender and Ksenzhek (1959), Bird et al. (1969), Johnson and Newman (1971), Gagnon (1973, 1974), and Tiedemann and Newman (1974). The merits of each experimental technique are often specific to the system currently under investigation. Of the effects mentioned previously, the most difficult to allow for is that associated with faradaic reactions. Little detailed information concerning the electrode kinetics of most porous electrodes is available. Also, the relative importance of faradaic reactions will change with the specific electrode composition and age (or cycling history). It is therefore desirable to employ experimental techniques which minimize the effects of faradaic reactions in the measurement of the double-layer capacity. We shall briefly mention three experimental techniques and refer the reader to de Levie (1967) and Posey and Morozumi (1966) for more complete analysis.

Bird et al. (1969) measured the double-layer capacity of battery electrodes by applying a potential step and integrating the resulting passage of current. A critical condition in this procedure is the absence of faradaic currents in the region of the applied potential step. Because of the distributed capacitance within the electrode, it is not possible merely to subtract the faradaic portion of the charging curve.

Gagnon (1973, 1974) has employed a triangular voltage sweep method. While he has shown the effects of distributed capacitance, faradaic reactions, and electrode thickness, best results are obtained when experiments are performed at reduced temperatures ( $-51^\circ\text{C}$ ), which minimize faradaic reactions.

Johnson and Newman (1971) have shown that the current response of a porous electrode to a step change in the potential yields, under certain circumstances, a nearly constant value of  $i\sqrt{t}$ , the product of the current density and the square root of time (also indicated by Ksenzhek and Stender, 1956a, Posey and Morozumi, 1966). A value

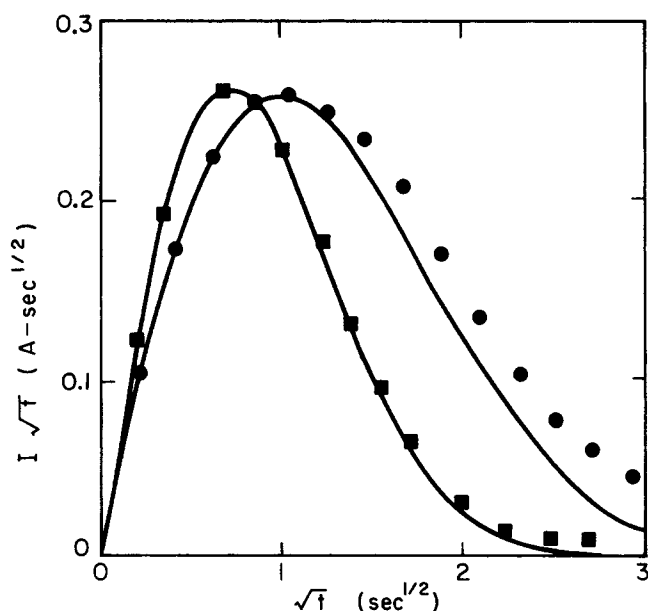


Fig. 4. Comparison of experimental and theoretical results for potentiostatic double-layer charging of porous  $\text{PbO}_2$  electrodes. Area =  $241 \text{ cm}^2$ ,  $L = 0.095 \text{ cm}$ , temperature =  $28^\circ\text{C}$ . ■ freshly prepared  $\text{PbO}_2$  electrode,  $\Delta V = 2.51 \text{ mV}$ ,  $\lambda = 1.33$ ,  $\alpha C = 23.33 \text{ f/cm}^3$ ; ● cycled  $\text{PbO}_2$  electrode,  $\Delta V = 1.52 \text{ mV}$ ,  $\lambda = 0.768$ ,  $\alpha C = 26 \text{ f/cm}^3$ . ( $\lambda$  is a ratio of the external resistance, ohm  $\text{cm}^2$ , to  $L/\kappa$ .) Solid curves are theoretical.

of the double-layer capacity can be inferred from this constant value of  $i\sqrt{t}$ . However, most porous electrodes have nonzero resistances which prevent the attainment of a constant value of  $i\sqrt{t}$  at short times, and the capacity begins to saturate at long times. Tiedemann and Newman (1974) used the same technique to study the  $\text{PbO}_2$  and  $\text{Pb}$  electrodes in  $\text{H}_2\text{SO}_4$  solution. However, a plot of  $i\sqrt{t}$  vs.  $\sqrt{t}$  yielded a maximum in  $i\sqrt{t}$ , and this value was used to obtain a value for the double-layer capacity. Figure 4 shows the comparison between theory and experiment for the charging curve of  $\text{PbO}_2$  in  $\text{H}_2\text{SO}_4$  solution. Emphasis on the maximum of this charging curve minimizes the ohmic effects at short times as well as the faradaic effects at long times. As faradaic reactions become more important, a positive displacement of the experimental curve from the theoretical curve is observed at long times. However, the shape of the curve near the maximum will remain relatively unchanged.

Johnson and Newman also demonstrated that specific adsorption of ions on a porous high-surface-area carbon electrode could be used to bring about a separation or concentration of soluble species. By alternating the applied potential at specified time intervals, a  $\text{NaCl}$  solution could be desalted during the adsorption cycle and concentrated during the desorption cycle. This technique constitutes a novel means of separation.

#### FLOW-THROUGH ELECTROCHEMICAL REACTORS

Flow-through porous electrodes possess inherent advantages over nonporous electrodes with flowing solutions or porous electrodes without flow. This has been well demonstrated by Kalnoki-Kis and Brodd (1973), who show increases in current by factors of  $10^2$  to  $10^4$  at a given overpotential. High specific interfacial area allows the attainment of relatively high volumetric rates of reaction, and the flowing solution eliminates or reduces mass-transport problems. Thick electrodes and low flow rates produce

relatively long contact times for treatment of very dilute solutions. A fluidized-bed electrode (Fleischmann et al., 1971) can replace the stationary porous matrix.

In modeling of the system for design purposes, there are a number of factors which might be included in the analysis. Many of these are already relevant for porous electrodes without flow, for example:

1. Should a straight-pore model or a homogeneous macroscopic model be used?
2. Should transport processes be described by dilute or concentrated electrolyte theory? How are conductivities and other transport properties to be estimated for porous media? Should ohmic losses in the solid matrix be included?
3. What are the kinetics of the reactions and the effects of side reactions?
4. Is the system isothermal?
5. Is operation steady or transient?

New factors are also introduced specifically for flow-through electrodes. These include:

1. Is the flow uniform through the electrode, or is there channeling?
2. What is the direction of flowing solution with respect to the counter electrode? The counter electrode can be upstream or downstream or it can be beside the working electrode. Two, rather than one, dimensional consideration of the distributions of concentration, current, and potential may be necessary.
3. How fast can reactants be transported from the flowing solution to the solid surface? Chemical-engineering correlations of mass-transfer coefficients in packed beds (Bird et al., 1960, pp. 411 and 679; Wilson and Geankoplis, 1966) are being extended to electrochemical situations by Yip (1973), Gracon (1974), and Appel (1974).

4. Do the flow patterns promote significant axial mixing? This dispersion effect is mathematically similar to diffusion and can be characterized by a dispersion coefficient  $D_a$ . Sherwood et al. (1975) have recently correlated available data on dispersion in packed beds and express their results in Figure 5 by plotting a Péclet number proportional to  $v/a(D + D_a)$  against a Reynolds number proportional to  $v/a\nu$ , with the Schmidt number\*  $\nu/D$  as a parameter. (For spheres, the effective particle diameter  $d_p$  on the graph is related to the specific interfacial area by  $d_p = 6(1 - \epsilon)/a$ .) Dispersion in the cross-flow, radial direction is also included. At low flow rates, axial mixing becomes less im-

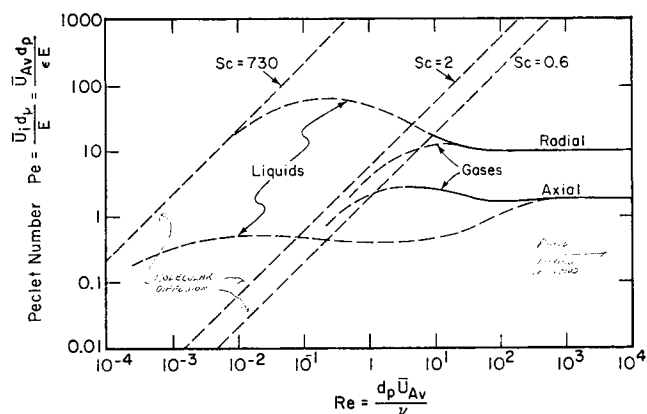


Fig. 5. Correlation of dispersion coefficients in packed beds,  $E = D + D_a$ . The asymptotes for molecular diffusion are based on  $\epsilon = 0.4$  and a tortuosity factor of 1.4.  $\bar{U}_{Av}$  is the superficial velocity  $v$ , and for spheres  $d_p = 6(1 - \epsilon)/a$ . (Sherwood et al., 1975).

\* The Schmidt number being based on the true molecular diffusion coefficient without any tortuosity factor.

portant than molecular diffusion, but the Reynolds number at which this occurs decreases as the Schmidt number becomes larger.

5. What is the approach to limiting current and the degree of conversion?

The extent to which any or all of the above are incorporated into the analysis is dependent on the specific system and given design and optimization requirements. Equations (8), (10), (19), (20), (23), and (33) facilitate the formulation of the problem, but to effect a solution may require various assumptions.

Austin et al. (1965) and Gurevich and Bagotskii (1963c, 1964) were the first to treat, in detail, the polarization behavior of flow-through porous electrodes. Assumptions employed were a homogeneous porous electrode in steady operation with uniform flow, a one-dimensional treatment, first-order electrode kinetics with no side reactions, negligible ohmic losses in the solid matrix and a constant solution conductivity, negligible dispersion, and negligible mass-transfer resistance. Solution was passed through from the back side, away from the counter electrode.

Johnson and Newman (1971) examined the adsorption and desorption of ions in a flow-through porous electrode as a means of desalting water. Their analysis included ohmic losses in the carbon matrix and transient operation. Schmidt and Gidaspow (1973) have presented a similar treatment.

Bennion and Newman (1972) emphasized the role of the mass transfer coefficient in their concentration of dilute solutions containing copper. Alkire and Ng (1974) analyzed the two-dimensional current distribution resulting from placement of the counter electrode parallel to the direction of flow within the working electrode. Other operational aspects of flow-through systems have been considered by Gurevich et al. (1968a, b), Budeka et al. (1968), Sohm (1962), Guillou and Buvet (1963), Sioda and Kemula (1972), and Wroblowa (1973).

Experimental investigations of single straight pore and micromesh electrodes have been conducted by Blaedel et al. (1963), Blaedel and Strohl (1964), Blaedel and Klatt (1966), Klatt and Blaedel (1967, 1968), and Blaedel and Boyer (1971, 1973). These studies are helpful in determining the correspondence between experiment and theory (since tortuosity and surface effects are small), as shown by Sioda (1974b). Further experimental investigations by Sioda (1968a, b, 1970) and Wroblowa and Saunders (1973) have helped to develop mechanistic criteria to treat these systems. Alkire and Mirarefi (1973) have analyzed the current distribution in a tubular electrode below the limiting current.

Carlson and Estep (1972) have studied removal of metal ions from aqueous waste streams, Beck and Giannini (1972) have considered effluent treatment, Roe (1964) has looked at electrochemical fractionation, and copper removal has been effected by Bennion and Newman (1972), Wenger et al. (1973), and Posey (1973).

Design and optimization is specific to the given system and have been discussed by Bennion and Newman (1972) and by Gurevich et al. (1968b). To illustrate the design principles outlined by Bennion and Newman, we examine the removal of  $\text{Cu}^{++}$  and  $\text{Pb}^{++}$ .

#### Qualitative Design Principles

1. We want to promote intimate contact between the electrode and the solution in order to carry out reactions to a high degree of completion. This calls for small flow channels and hence for a flow-through porous electrode.

2. Carrying reactions to a high degree of completion also calls for operation at the limiting current so that the

concentration at the walls of the pores is close to zero. This also brings about considerable simplification in the design calculations, since it decouples the potential distribution from the mass transfer rates and current distribution.

#### Quantitative Design Principles

1. We want to avoid side reactions. These could range from unwanted evolution of hydrogen or oxygen to competing reactions or subsequent reactions in electro-organic synthesis. Consequently, the potential variation in the solution phase should not exceed a certain limit, one or two tenths of a volt in moderately sensitive cases. For high degrees of completion, the design equation is

$$|\Delta\Phi|_{\max} = \frac{nF v c_0}{\kappa} \frac{v}{ak_m} \quad (48)$$

which can be regarded as the product of a superficial current density ( $nFvc_0$ ) with the reciprocal of the effective conductivity ( $1/\kappa$ ) and an effective depth of penetration of the reaction into the electrode ( $v/ak_m$ ). The mass transfer coefficient  $k_m$  itself depends on the velocity so that  $|\Delta\Phi|_{\max}$  is proportional to the velocity to about the 1.5 power.

In practice, we would use this equation to determine the maximum permissible velocity or throughput which can be achieved while avoiding side reactions and yet operating near limiting current. Note how the difficulty of the problem (or separation process) is governed by the ratio  $c_0/\kappa$  of the reactant concentration to the conductivity and by the specific interfacial area  $a$  of the electrode. (After allowance for the dependence of  $k_m$  on  $a$ ,  $|\Delta\Phi|_{\max}$  is proportional to  $a$  to about the -1.5 power.)

2. The thickness of the electrode is now determined by the required degree of reaction. This is given by

$$L = \frac{v}{ak_m} \ln \frac{c_0}{c_b^L} \approx \frac{\sqrt{v} Sc^{1/6}}{a^{1.5} \sqrt{D}} \ln \frac{c_0}{c_b^L} \approx \left( \frac{\kappa \Delta\Phi_{\max}}{nF c_0} \right)^{1/3} \frac{Sc^{1/12}}{a D^{1/3}} \ln \frac{c_0}{c_b^L} \quad (49)$$

Costs of course depend on how  $c_0$ ,  $c_b^L$ ,  $\kappa$ , and  $a$  affect  $v$  and  $L$ . Comparisons are given in Table 1 for the lead and copper systems. As the feed concentration is increased by a factor of 415, the cost per unit volume goes up by a factor of 90 while the cost per unit mass goes down by a factor of 4.6. The pumping power makes a dramatic in-

TABLE 1. OPERATING CONDITIONS, DESIGN RESULTS, AND COSTS FOR REMOVAL OF LEAD AND COPPER IONS FROM GIVEN SOLUTIONS

	Pb system		Cu system	
Feed concentration, mg/liter	1.45		667	
Product concentration, mg/liter	0.05		1	
Solution conductivity, mho/cm	0.8		0.17	
Allowable potential variation, V	0.1		0.2	
Specific electrode area, $\text{cm}^{-1}$	25		25	
Superficial velocity, $\text{cm/s}$	0.64		0.0036	
Electrode thickness, cm	60		5	
Time to plug, days	377		5	
	Pb system		Cu system	
	$\text{\$/kgal}$	$\text{\$/lb.}$	$\text{\$/kgal}$	$\text{\$/lb.}$
Electrode capital cost	0.2222	0.1836	26.5	0.0529
Operating labor	0.0218	0.0180	4.2	0.0083
Electrical energy	0.0021	0.0018	3.3	0.0066
Pumping energy	0.132	0.109	0.014	0.00003
Total	0.38	0.31	34	0.068

crease in importance for dilute solutions.

A variety of processes of potential interest for application of the concept of flow-through, porous-electrode electrochemical reactors is as follows:

1. Removal of electropositive cations by electrodeposition.

- a. Cu 600 ppm to < 1 ppm.
- b. Pb 1.45 to 0.05 ppm from  $\text{H}_2\text{SO}_4$  solutions.
- c. Hg 10 to 0.01 ppm from solution 280 g/l NaCl.
- d. Ag processing of waste photographic emulsions.
- e. Au from waste plating solutions.

2.  $\text{Fe}^{++}$  to  $\text{Fe}^{+++}$ . Acid mine drainage waters.

3. Oxidation of organic pollutants and of  $\text{CN}^-$  (24 to 0.1 ppm).

4. Oxidation of organic surfactants. Reduction of foaming in Solvay process for manufacture of  $\text{Na}_2\text{CO}_3$ .

5. Electro-organic synthesis where the need for careful control of potential may have ruined attempts at scale up. Many of these—both oxidations and reductions—are related to water pollution abatement. Others may have independent economic incentives.

Some of these processes raise questions about new aspects of the system design such as

1. How to design a counter electrode to carry out a gas-evolution reaction.
2. How to separate anode and cathode processes.
3. How to regenerate the electrodes in the case of lead deposition.
4. How to carry out both reduction and oxidation on a waste stream.
5. How to balance oxidation needed in one process with reduction needed in a separate process.

## EXPERIMENTAL INVESTIGATIONS

Current distribution within an electrode has been determined by measuring the distribution of discharged material through the interior (see, for example, Brodd, 1966; Bro and Kang, 1971; Nagy and Bockris, 1972; Alkire, 1968; Euler and Horn, 1965; Bode and Euler, 1966a, b; Bode et al., 1966). This determination involves a wash-dry operation followed by electrode sectioning, and this procedure can result in a net reduction and a redistribution of material within the electrode. Sectioning the electrode also results in averaging the material in question over a non-zero thickness and may result in an inaccurate picture of the real current distribution.

Current distribution can also be inferred by measuring the potential distribution with reference electrodes located in the electrode (Daniel-Bek, 1948; Brodd, 1966) or by using a sectioned electrode and directly measuring the current in each element (Coleman, 1951). However, sectioned electrodes are usually inferior to sectioning because of the small distance involved, an exception being the  $\text{MnO}_2$  electrode (Coleman, 1951). Studies on simulated single pores (Will and Hess, 1973) have helped to examine microstructure problems. Gagnon and Austin (1971) formed a composite  $\text{Ag}-\text{Ag}_2\text{O}$  electrode from five thin sections and determined the current distribution by disassembling and completing the discharge in each section. Panov et al. (1969) used a composite electrode of 15 sections with provision for varying both solid and solution phase resistance. The results are in good agreement with the calculations of Daniel-Bek (1966) and of Newman and Tobias (1962).

Most investigations have tended to support the predictions of porous-electrode theory. Haebler et al. (1970) reported results at odds with the predictions of Stein

(1958). However, Simonsson (1973a) showed that this discrepancy was the result of their wash-dry procedure.

Haebler et al. (1970) and Szpak et al. (1966) removed mass transport limitations by flowing the solution through the electrode. Such effects had been examined already by Liebenow (1897). Recently, flow-through electrodes have emerged as a potentially useful industrial process. Bennion and Newman (1972) thus concentrated copper solutions. Carlson and Estep (1972) used flow-through porous electrodes to remove trace metal impurities from waste streams. Austin et al. (1965) and Wroblowa and Saunders (1973) have examined the reactions of organic and inorganic materials. Sioda (1970, 1971, 1972a, b, c, 1974a) has examined flow-through electrodes with an emphasis on electroanalytical applications.

Only a small number of experimental porous electrode studies have yielded kinetic information (Posey and Misra, 1966; Austin and Lerner, 1964), the potential-time discharge behavior (Simonsson, 1973b, c), or the electrochemically active surface area (Euler, 1961). Information in these areas is needed to refine the models which are being developed.

## ESTIMATION OF PHYSICAL PROPERTIES

The porosity of an electrode plays a major role in determining its polarization behavior. The void volume contained within the electrode provides not only intimate contact between solution and solid phases, as well as a reservoir of soluble species available for consumption, but also the necessary space for storage of solid products of reaction. The effective solution and solid phase conductivities and the solution diffusion coefficient are found to be functions of the porosity. The correspondence between theory and experiment is strongly dependent on the values selected for the effective conductivities and diffusion coefficients as well as their functional dependence on porosity. Therefore, it is important that these parameters be either measured experimentally or predicted from appropriate equations.

Meredith and Tobias (1962) have reviewed extensively conduction in heterogeneous media. Equations were derived which predict the effective conductivity of solutions in multiphase dispersions as a function of the volume fraction occupied by the solution. The utility of these equations lies in their ability to account for changes in the effective solution conductivity of porous electrodes undergoing structural changes during testing. Their results suggest that the effective conductivity can be found by multiplying the bulk conductivity times the porosity raised to the three-halves power. Gagnon (1973) showed that this relationship is in good agreement with experimental results. Schofield and Dakshinamurti (1948) have shown that the same porosity factor can be used for the diffusion coefficient. (The effective diffusion coefficient considered here is  $\epsilon D_i$  in terms of the diffusion coefficient introduced in Equation (20).) Ksenzhek, Kalinovskii, and Baskin (1964) measured the conductivity of 1.0N sodium hydroxide solution in porous nickel and carbon electrodes. Their results suggest that the effective conductivity of the contained solution is proportional to  $\epsilon^3$  rather than  $\epsilon^{1.5}$ , as suggested by Meredith and Tobias.

Direct measurement of the effective conductivity of a solution in an inert porous material can be readily accomplished and offers a check on the correlations mentioned above. However, since porous electrodes have an electronically conducting solid phase, the passage of alternating or direct current through the electrode (with the electrode acting as an inert separator) will be affected by the amount of current which passes through the solid phase by way of

double-layer charging or faradaic reactions. Posey and Misra (1966) have analyzed bipolar porous electrodes to show how to correct the measured conductivity for the presence of faradaic reactions. Experimental studies by Romanova and Selitskii (1970) and by Simonsson (1973a) have shown the importance of gas bubbles on the measurement. Oldham and Topol (1967, 1969) have developed equations for potentiostatic and galvanostatic diffusion studies on porous media and have obtained experimental verification (Topol and Oldham, 1969) of their predictions.

The value of the true electrochemically active interfacial area is difficult to determine. A BET measurement reflects all the area present, including matrix, binders, and non-conducting fuel. Tiedemann and Newman (1974) and Gagnon (1973) have developed experimental techniques, involving double-layer charging, to assess the electrochemically active area. Katan and Bauman (1974) have shown how various geometric variables of a porous electrode can be used to estimate the specific interfacial area.

## CONCLUSIONS

The theory of the operation and behavior of porous electrodes has been developed to the point where almost any system can be treated. In particular, equations were developed to provide the bases for examining the behavior of specific systems such as primary and secondary batteries, adsorption and double-layer charging, and flow-through electrochemical reactors.

Experiments have verified the predictions of nonuniform current distribution in several types of porous electrodes, but experimental information on the transient behavior of porous electrodes is scarce. The polarization expression applicable to a given system is subject to refinement to account for the morphology of the electrode, the formation of covering layers or of crystallites of sparingly soluble species, and the transport from such sparingly soluble phases to the site of the charge-transfer process.

Areas which remain to be examined in greater detail are: (1) complete analysis of an entire electrochemical cell; (2) prediction of the entire polarization curve for a given battery; (3) dynamic behavior of flow-through electrochemical reactors; (4) complete optimization of a given electrochemical system.

## ACKNOWLEDGMENT

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## NOTATION

$a$	= specific interfacial area, $\text{cm}^{-1}$
$A_0$	= constant defined by Equation (12)
$c$	= concentration of binary electrolyte, $\text{mole}/\text{cm}^3$
$c_i$	= concentration of species $i$ per unit volume of solution, $\text{mole}/\text{cm}^3$
$c_i^0$	= reference or bulk concentration, $\text{mole}/\text{cm}^3$
$c_0$	= solvent concentration, $\text{mole}/\text{cm}^3$
$c_0$	= feed concentration to flow-through electrode, $\text{mole}/\text{cm}^3$
$c_b^L$	= exit concentration for flow-through electrode, $\text{mole}/\text{cm}^3$
$c_T$	= total solution concentration, $\text{mole}/\text{cm}^3$
$C$	= differential double-layer capacity, $\text{f}/\text{cm}^2$
$d_p$	= effective particle diameter of bed packing, $\text{cm}$
$D$	= diffusion coefficient of electrolyte, $\text{cm}^2/\text{s}$
$D_a$	= dispersion coefficient, $\text{cm}^2/\text{s}$
$D_i$	= diffusion coefficient of species $i$ , $\text{cm}^2/\text{s}$
$E$	= $D + D_a$ , $\text{cm}^2/\text{s}$

$f$	= represents current density $i_n$ in the polarization equation, $\text{A}/\text{cm}^2$
$F$	= Faraday's constant, $96487 \text{ C}/\text{equiv}$
$i_0$	= exchange current density, $\text{A}/\text{cm}^2$
$i_1$	= superficial current density in the matrix, $\text{A}/\text{cm}^2$
$i_2$	= superficial current density in pore phase, $\text{A}/\text{cm}^2$
$i_n$	= transfer current per unit of interfacial area, $\text{A}/\text{cm}^2$
$I$	= superficial current density to an electrode, $\text{A}/\text{cm}^2$
$j$	= $\nabla \cdot i_2$ , transfer current per unit volume of electrode, $\text{A}/\text{cm}^3$
$j_{in}$	= pore-wall flux of species $i$ , $\text{mole}/\text{cm}^2\text{-s}$
$k_1$	= reciprocal penetration depth for diffusion, see Equation (46), $\text{cm}^{-1}$
$k_m$	= coefficient of mass transfer between flowing solution and electrode surface, $\text{cm}/\text{s}$
$L$	= thickness of porous electrode, $\text{cm}$
$M_i$	= symbol for the chemical formula of species $i$
$M_i$	= molecular weight of species $i$ , $\text{g}/\text{mole}$
$n$	= number of electrons transferred in electrode reaction
$\mathbf{n}$	= normal unit vector
$N_i$	= superficial flux of species $i$ , $\text{mole}/\text{cm}^2\text{-s}$
$q$	= surface charge density on solid side of double layer, $\text{C}/\text{cm}^2$
$R$	= universal gas constant, $8.3143 \text{ J}/\text{mole-deg}$
$s_i$	= stoichiometric coefficient of species $i$ in electrode reaction
$Sc$	= Schmidt number, $\nu/D$
$t$	= time, $\text{s}$
$t_i^0$	= transference number of species $i$ with respect to the solvent velocity
$T$	= absolute temperature, $^\circ\text{K}$
$u_i$	= mobility of species $i$ , $\text{cm}^2\text{-mole}/\text{J-s}$
$U'$	= $\Phi_1 - \Phi_2$ , $\text{V}$
$\mathbf{v}$	= superficial fluid velocity, $\text{cm}/\text{s}$
$\mathbf{v}^\square$	= superficial volume average velocity, $\text{cm}/\text{s}$
$\mathbf{v}^\star$	= molar average velocity, $\text{cm}/\text{s}$
$V$	= $\Phi_1(L) - \Phi_2(0)$ , volt
$\bar{V}_i$	= partial molar volume of species $i$ , $\text{cm}^3/\text{mole}$
$x$	= distance through porous electrode, $\text{cm}$
$z_i$	= valence or charge number of species $i$

## Greek Letters

$\alpha_a$	= transfer coefficient in anodic direction
$\alpha_c$	= transfer coefficient in cathodic direction
$\beta$	= $\alpha_a F/RT$ or $-\alpha_c F/RT$
$\gamma_i$	= dimensionless diffusion parameter
$\Gamma_i$	= surface concentration of species $i$ , $\text{mole}/\text{cm}^2$
$\delta$	= dimensionless current density defined in Equation (37)
$\epsilon$	= porosity or void volume fraction
$\eta_s$	= surface overpotential, $\text{V}$
$\kappa$	= effective conductivity of solution, $\text{mho}/\text{cm}$
$\kappa'$	= modified solution conductivity, $\text{mho}/\text{cm}$
$\mu_e$	= chemical potential of electrolyte, $\text{J}/\text{mole}$
$\nu$	= kinematic viscosity of flowing solution, $\text{cm}^2/\text{s}$
$\nu$	= square root of a dimensionless exchange current; see Equation (38)
$\nu_+, \nu_-$	= numbers of moles of cations and anions produced by the dissociation of a mole of electrolyte
$\rho_i$	= density of a solid phase of species $i$ , $\text{g}/\text{cm}^3$
$\sigma$	= effective conductivity of the solid matrix, $\text{mho}/\text{cm}$
$\Phi_1$	= electric potential in the matrix, $\text{V}$
$\Phi_2$	= electric potential in the solution, $\text{V}$

## Subscripts

0	= solvent
e	= electrolyte
+	= cation
-	= anion



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## Oscillating Behavior on Distillation Trays-II

This paper describes an extension of an earlier study on oscillations which can develop on distillation trays. The oscillations take the form of violent lateral movements of the gas/liquid biphasic, and they are generally undesirable for good column performance. It has been found that lower density gases need higher velocities to initiate oscillation, and vice versa for higher densities. The predictive method for the onset of oscillations proposed previously appears to remain valid for the range of gas density covered, and for small hole size trays. The presence of oscillations has been shown to increase weeping significantly.

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#### SCOPE

The objective of this work was to extend the study by Biddulph and Stephens (1974) of the phenomenon of oscillations on sieve trays. The dimensionless group which was proposed earlier as a criterion for the onset of oscillations was based on the work of Hinze (1965) and on dimensional analysis. The group did appear to have consistent critical values for full-wave oscillation and half-wave oscillation for the results then available. However all these

results were on the system air/water, and so the dependence on gas density could not be confirmed. In this extension of the work, the apparatus was modified to allow various gas mixtures to be used. This was achieved by converting the open system used previously into a sealed, closed-circuit system. Mixtures of helium and air of various compositions were used to obtain densities lower than that of air. Mixtures of carbon dioxide and air were used