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ABSTRACT

A theoretical model is proposed for the description of flooded porous metal electrodes which undergo anodic dissolution by electrochemical reaction. Equations are developed to represent the pseudo-steady state which prevails during dissolution after the concentration gradients have become fully established within the pores. The analysis leads to an understanding of how mass transfer, kinetic and geometric parameters of the system determine the electrode overpotential and its change during dissolution. The most uniform current distributions are predicted to occur not at vanishingly small currents but at finite anodic currents because of mass transfer limitations to the cathodic back reaction. Thus, for a range of anodic currents, an increase of applied current will result in a more uniform distribution of the electrochemical reaction throughout the porous electrode. Calculations illustrating the behavior are presented for the acid-copper system.

Introduction

Electrodes which are porous have come into widespread use in electrochemical energy conversion devices because, in these, the electrochemical reaction takes place with a higher rate per unit volume and is accompanied by a lower polarization than would be possible with non-porous electrodes. Accordingly almost all batteries and fuel cells employ porous electrodes. In batteries the electrode pores are flooded with liquid electrolytic solution, and reactants and/or products are incorporated in the solid electrode matrix. Thus, during operation, the composition and configuration of the solid material changes, leading to departures from behavior that might be expected for electrodes with invariant matrices. The nature of such changes, which are dependent on the electrode system involved, can be very complicated indeed. In this work an analysis has been conducted of a simple class of electrodes experiencing structural change during operation: porous metal anodes undergoing electrochemical dissolution. The investigation of this type of electrode can illuminate some of the salient effects of structural changes in battery electrodes and can serve as a basis for extension of model studies of systems encountered in batteries.

The dissolving metal anode, of course, involves a relatively simple type of structural change. No changes in solid composition are involved. The behavior of most battery electrodes is far more complicated, but the state of description of such systems has not yet advanced sufficiently far to embrace these more complicated events. Theoretical analyses to date have proceeded by one of two routes. In the first, an idealized geometrical structure of the porous body is assumed and is taken into consideration when equations are derived for the current and potential distributions (1, 2, 3). This

"microscopic" approach has been found to lead to severe mathematical difficulties and has been restricted to extremely simple geometries. The second method ignores the detailed structure of the porous electrode and, rather, treats the porous electrode as a pseudo-homogeneous region in which there is transfer of current between electronic and ionic modes of conduction according to basic laws of transport phenomena and electrode kinetics. This "macroscopic" approach has been applied to electrode behavior in the initial state without concentration gradients (4, 5, 6, 7, 8, 9, 10), during the mass transfer transients (11), and in the steady state where concentration gradients are fully established (11, 12, 13). As more sophisticated models were examined, the solution of the equations was found to be more conveniently carried out by numerical methods implemented by high-speed digital computers (11).

To date, no theoretical analysis has been reported which takes into consideration the variation of electrode structure with extent of reaction. The macroscopic theory presented here examines the behavior of porous metal electrodes that are undergoing dissolution by anodic reaction and predicts the external electrode polarization and the electrode porosity distribution as a function of the extent of reaction.

The operation of battery systems involves other effects beyond those considered in the theoretical model used in this work. Typically, sparingly soluble salts take part in the reactions during cycling. These salts may be insulators or semiconductors and hence may greatly affect the potential distribution within the electrode. There may be composition gradients in the solid phase (for instance $Ag/Ag_2O/AgO$) and, furthermore, electronic transport in the solid phase may be important (as in Pb electrodes which have high ohmic resistance). Also, reactions may be locally nonuniform, and geometrical effects

of crystal growth may be involved. Nevertheless, the theoretical model presented below represents an advance relative to existing treatments in the literature and should be useful in leading to some insight into more complex systems.

Model Formulation

The mathematical model for a dissolving porous anode is based on consideration of a porous metal plate whose accessible void spaces are completely filled with an aqueous electrolyte. On one side of the porous plate the pores are blocked (or a center of symmetry exists), and the other side (the face) is in contact with the electrolytic solution, which also fills the pores. There is no forced flow of solution through the pores. A second (counter) electrode is also in the solution but is of no concern in this model and serves only to complete the electrochemical circuit. With passage of anodic current through the porous electrode, the metal dissolves with formation of a soluble salt. The local rate of anodic dissolution varies from place to place within the porous electrode because the various positions are not equally accessible to the current and the reacting species transported in the electrolyte. The distribution of the reaction depends upon the mass transfer, kinetic and geometric characteristics of the particular system.

When anodic current is switched on, two major changes begin to take place.[1] Because of the removal of dissolved product species from the pore is transport controlled, as is also the passage of current and movement of nonreacting ions in the electrolyte, the potential and concentrations of species in the solution

[1] During the first few milliseconds the electrical double layer becomes established. We shall not be concerned with the electrode behavior during this brief period of double layer charging.

within the pores change from the initially uniform values and become more or less unevenly distributed throughout the pores. Typically this mass transfer transient process is completed within a period of ten seconds to an hour, depending upon the system (11). Secondly, and simultaneously, the geometry of the porous metal matrix changes owing to its dissolution by anodic reaction. As the nature of the electrode structure thus changes, the potential and concentration distributions also change, and these changes continue to take place as long as current is passed.

When anodic current thus passes through the porous metal electrode, the current in the metal is carried by electrons and the current in the solution is carried by the ions. The conversion from the electronically to the ionically conducting "phase" takes place throughout the porous electrode by virtue of the electrochemical reaction. If the local concentrations and potentials are known in both phases, the local reaction rate may be calculated, in principle, by a relation which suitably describes the kinetics of the electrode process. In turn, the local concentrations and potentials may be obtained by solving the equations of transport in each phase. Thus the local reaction rate may be determined throughout the electrode.

During the first moments of operation, the reaction distribution changes principally because of the production of ionic reaction products whose removal in the solution phase from the porous electrode is transport restricted. Along with this mass transfer transient process, the reaction distribution changes at some other rate owing mainly to the changes in structure caused by dissolution. The characteristic times of these two effects are usually different, the former being much faster. Consequently, after the mass transfer transient has been essentially completed, the reaction distribution continues to change,

and it becomes a very good approximation to determine the rate of change solely from the effects of the structural dissolution. This is the pseudo-steady state approximation that will be invoked in the present theory.

The equations describing electrode behavior arise from transport relations and electrode kinetic expressions. In definition of the model it is necessary to introduce a number of simplifying assumptions to facilitate the required calculations:

1) The one-dimensional macroscopic approach is applicable; pore dimensions are assumed to be small with respect to distances over which significant changes take place within the electrode.
2) The electrode operation under consideration takes place in the pseudo-steady state. Behavior during the mass-transfer transient is ignored.
3) The electrical double layer can be disregarded. The pore dimensions are large compared to those of the double layer, and the time variations are slow compared to the rate of establishment of the double layer.
4) The motion of solute species in the electrolytic solution is adequately described by the equations of dilute solution theory. The transport parameters are constant, and hydrodynamic flow in the pores is due only to the net change of electrode and electrolyte volume with the extent of reaction. The density of the electrolytic solution is constant throughout the pores, and the metallic electrode structure is isopotential.
5) The only electrochemical reaction is the anodic dissolution of the metal electrode to form ions having a single charge number, and the kinetic behavior of the reaction is adequately characterized by an expression of the Volmer form (14).

6) There are no insoluble substances within the pores.

7) The pores are circular cylinders which all have the same size at the onset of dissolution.

8) Mass transfer resistances external to the porous electrode can be disregarded.

9) The system is isothermal.

The analysis of electrochemical systems by the equations of transport as delineated, for instance, by Levich (15) and by Newman (16), has been applied to the formulation of a macroscopic porous electrode model by Grens and Tobias (11). It is here extended to account for the changes in matrix properties accompanying anodic dissolution of the matrix. Under the conditions described above, the conservation of solute species in the pseudo-steady state is described by

$$c_i \frac{\partial a}{\partial t} = - \frac{\partial}{\partial y} (N_i a) + S_i \qquad (1)$$

In this equation the left hand side represents the amount of species i associated with changes in pore volume while the terms on the right hand side are the divergence of the species flow (flux times local pore cross section) and the reaction source, respectively. For non-reacting species, the only net movement is that which must take place in order to fill the void volume created by the dissolving metallic phase. The time rate of change of the pore cross-sectional area may be related to the convective velocity by use of the relation for conservation of mass in the pores which, in the pseudo-steady state, is

$$\rho_s \frac{\partial a}{\partial t} = - \frac{\partial}{\partial y}(\rho_s v a) + R \quad . \qquad (2)$$

The spatial coordinate, y, is taken to be zero at the back of the porous electrode and has the value of +d at the mouth of the pores (face of the porous layer). The flux of solute species in the one dimensional electrolytic solution is given by the dilute solution expression

$$N_i = - D_i \frac{\partial c_i}{\partial y} - z_i D_i \frac{F}{RT} c_i \frac{\partial \phi}{\partial y} + v c_i \quad . \tag{3}$$

For the electrode reaction which occurs in the pores, with the dissolved metal ion being designated species 1,

$$\nu_1 M \rightarrow \nu_1 M^{z_1} + ne^- \quad , \tag{4}$$

the pseudo-homogeneous species source term is

$$S_1 = - \frac{\ell \nu_1}{nF} j \quad , \tag{5}$$

where j is the local reaction (transfer) current density. Other source terms are absent. The transfer current density is in turn related to local concentrations and potential by the kinetic expression associated with the dissolution reaction, here the Volmer form :

$$j = i_o \left[e^{- \frac{\alpha_a nF}{RT}(\phi - \phi_e)} - \frac{c_1}{c_1^\infty} e^{\frac{\alpha_c nF}{RT}(\phi - \phi_e)} \right] \quad . \tag{6}$$

The pseudo-homogeneous mass source term for the pore space is

$$R = \frac{m_1 \ell}{nF} j \quad . \tag{7}$$

Substitution of Eqs. (2), (3), (5), (6), and (7) into Eq. (1) eliminates the time derivative term for pore area and incorporates the definitions of fluxes and sources in the species conservation equations. With neglect of the pseudo-homogeneous mass source term, and with assumption of constant solution density, these equations are:

$$D_i \frac{d^2}{dy^2}(c_i a) + \frac{z_i D_i F}{RT}\frac{d}{dy}\left(c_i \frac{d\phi}{dy}\right) - vac_i = \frac{\nu_i \ell}{nF} i_o \left[e^{-\frac{\alpha_a nF}{RT}(\phi-\phi_e)} - \frac{c_l}{c_l^\infty} e^{\frac{\alpha_c nF}{RT}(\phi-\phi_e)} \right] - c_i \frac{d}{dy}(va), \qquad \nu_i = 0 \text{ for } i \neq 1. \tag{8}$$

A conservation equation is written for each of the solute species i. These equations, along with the electroneutrality approximation,

$$\sum_i z_i c_i = 0 \quad , \tag{9}$$

are sufficient in number for the calculation of the concentrations and the potential, provided that the pore area, pore perimeter and convective velocity have been specified. For the system considered here, these are determined by the effect of local reaction on the solid matrix.

With the assumption that the pores are circular cylinders, the radius will change at a rate proportional to the local reaction rate according to

$$\frac{d}{dt}(r^2) = \frac{2\overline{V}}{nF} jr \quad . \tag{10}$$

By integration of Eq. (10), the area and perimeter of the pores may be obtained at any one time during dissolution. The average local velocity past a point within the electrode is derived from a mass balance and is

$$v(y) = \frac{m_1}{nF\rho_s a} \int_0^y \ell(1 - \frac{\rho_s}{\rho_m}) j \, dy \quad , \tag{11}$$

when the density of the electrolytic solution is constant. This equation indicates that the induced velocity arises from the difference between the densities of the solution and the metal, and that the velocity at position y depends upon reaction in the portion of the electrode between that point and the back of the electrode.

The model is completely described when the appropriate boundary and initial conditions are specified. Prior to dissolution the pores are assumed to be of identical size and shape,

$$a = a_o \quad \text{at } t = 0 \quad . \tag{12}$$

At the rear of the pores, the flux of each species is zero,

$$N_i = 0 \quad \text{at } y = 0 \quad . \tag{13}$$

At the entrance of the pores, the concentration of each solute species is equal to its value in the external electrolytic solution,

$$c_i = c_i^{\infty} \quad \text{at } y = d, \; i \neq 1 \quad . \tag{14}$$

The current density in the electrolyte at the mouth of the pores is defined as the sum of the individual ionic fluxes according to

$$i = F\sum_i z_i N_i \ . \tag{15}$$

If the metal electrodes were not dissolving, then the current entering the pores could be solely attributed to the flux of the reacting ion. However, since the liquid volume within the pores is increasing by dissolution, that portion of the flux of the reacting ion passing into the electrode only to fill the void spaces is accompanied by equivalent counter ions and thus will not contribute to the current. The appropriate boundary condition in this case, derived by integration of the conservation equation over the entire electrode, is

$$i = -z_1 F D_1 \frac{dc_1}{dy} - \frac{z_1^2 F D_1}{RT} c_1 \frac{d\phi}{dy} + \frac{1}{a_f}\int_0^d va\, dc_1, \qquad \text{at } y = d \tag{16}$$

In many instances, the integral term will be negligibly small with respect to the sum of the other two terms and thus may be deleted from consideration. This was the case in the system for which numerical results were obtained for this paper.

The treatment of the equations is more convenient if the variables are made dimensionless. The following dimensionless variables are conveniently defined:

$$Y = \frac{y}{d} \quad , \qquad C_i = \frac{c_i}{c_{ref}} \quad , \qquad \Phi = \frac{F}{RT}(\phi - \phi_e) \quad ,$$

$$V = \frac{vnF}{i^* \bar{V}} \quad , \qquad A = \frac{a}{a_o} \quad , \qquad L = \frac{\ell}{\ell_o} \quad ,$$

$$I = \frac{i}{i^*} \quad , \qquad J = \frac{\ell d}{i^* a_f} j \quad , \qquad \tau = \frac{\bar{V} i^* a_f}{nFd} t$$

When these are introduced in Eqs. (8) and (16), the following dimensionless groupings of the system parameters arise:

$$\beta = \frac{i^* a_f d}{nFc_{ref} D_{ref} a_o} \quad , \qquad \xi = \frac{i_o d^2 \ell_o}{nFc_{ref} D_{ref} a_o} \quad ,$$

$$\zeta = \frac{i^* a_f \bar{V} d}{nFD_{ref} a_o} \quad , \qquad \gamma_i = \frac{c_i^\infty}{c_{ref}} \quad , \qquad \pi_i = \frac{D_i}{D_{ref}}$$

With use of the notation prime (') to denote differentiation with respect to the spatial variable Y, the dimensionless equations which describe the pseudo-steady state model become

$$(C_i' A)' + z_i (C_i A \Phi')' - \frac{\zeta}{\pi_i A_f}(C_i' A V)$$

$$= \frac{\nu_i \xi L}{\pi_i} \left[\exp(-\alpha_a n \Phi) - \frac{C_1}{\gamma_1} \exp(\alpha_c n \Phi) \right] \quad , \tag{17}$$

$$\sum_i z_i C_i = 0 \quad , \tag{18}$$

$$A = 1 + \int_0^\tau J \, d\tau \quad , \tag{19}$$

$$V = \left(\frac{\rho_m}{\rho_s} - 1\right) \frac{A_f}{A} \int_0^Y J \, dY \quad . \tag{20}$$

Since the pores are circular cylinders, $L = \sqrt{A}$. The boundary conditions become

$$C_i' + z_i C_i \Phi' = 0 \quad \text{at } Y = 0 \quad , \tag{21}$$

and

$$\left.\begin{aligned} C_i &= \gamma_i \quad (i \neq 1) \\ -\frac{n\beta}{z_1 \pi_1 A_f} &= C_1' + z_1 C_1 \Phi' \end{aligned}\right\} \quad \text{at } Y = 1 \quad . \tag{22}$$

The calculations in this study were made with neglect of the integral term in Eq. (16), resulting in a boundary condition of the form of Eq. (22).

The mathematical model described above has extended previous treatments by accounting for two phenomena which take place during electrolytic dissolution: the change in specific surface area, and the convective motion arising from volumetric changes.

Solution of Equations

The solution of the set of equations and boundary conditions which describe the porous electrode model was carried out by a computer-implemented numerical technique. In principle, the calculation was accomplished in a stepwise manner, with use of finite difference methods for solution of the differential equations at each step. First, the conservation and electroneutrality equations, (17) and (18), were solved without the convection term and with constant porosity. The first approximation to the local convective velocity was then calculated by Eq. (20). Conservation and electroneutrality equations were again solved with use of the velocity distribution now at hand; these results corresponded to the

conditions prevailing within the electrode at the end of the mass transfer transient but before appreciable dissolution had taken place. Then the calculations were made for specified time intervals during the pseudo-steady state dissolution. With use of Eqs. (19) and (20), the pore area (i.e., porosity) distribution and the convective velocity distribution were calculated. With use of these new distributions, the conservation and electroneutrality equations were again solved, and the sequence repeated for as many time intervals as required.

The central problem of these calculations was the simultaneous solution of the species conservation expressions along with the electroneutrality condition. These coupled nonlinear ordinary differential equations were first linearized about an approximate solution and then put into finite difference form. The resulting set of tridiagonal matrices was solved by use of a computer-implemented technique described by Newman (17). The solution of the nonlinear problem was obtained by iteration with successive correction of the approximate solution.

Results and Discussion

The theoretical model developed above was used for generating predictions regarding the behavior of one porous electrode system. Ultimately it is intended that these model predictions be compared with the results of dissolution experiments that have been undertaken in a related project (18). Consequently the dissolution of porous copper anodes in acidified copper sulfate has been examined. For this system there are two alternate models for the electrolyte composition (and thus for electrolyte transport): the sulfate model (Cu^{+2}, H^+, SO_4^{-2}) and the bisulfate model (Cu^{+2}, H^+, HSO_4^-). For solutions having a larger concentration of sulfuric acid than copper sulfate the bisulfate model gives a more

accurate prediction of the solution conductivity than does the sulfate model, and thus was chosen for these calculations. The system parameters are given in Table I.

For the moment, consider the state which exists after the mass transfer transient has decayed but before significant dissolution has taken place. Figure 1 shows the corresponding distribution of reaction rate throughout the porous electrode for various anodic values of applied potential, Φ_f. From this figure it may be seen that this initial steady state current distribution varies with applied potential, and that as the anodic potential is increased the reaction distribution generally becomes more uniform. For the case at hand, increasing $-\Phi_f$ above 3.0 renders the distribution still more uniform in the depth of the electrode while, nearer the pore entrance, the distribution begins to become more nonuniform.[2] This interesting situation may be understood by the following reasoning. Since the electrode consists of copper metal, the anodic reactant (the copper atom) is available in unlimited quantity whereas the cathodic reactant (the copper ion in solution) is not. Therefore the cathodic (back) reaction suffers from mass transfer limitations which do not hinder the anodic reaction. Consequently, at the same value of absolute potential, the cathodic reaction will be less uniformly distributed through the electrode. This tendency for the cathodic reaction to be less uniformly distributed carries over into the region of low anodic current where the cathodic back-reaction still occurs to an appreciable extent. Thus the most uniform reaction distribution is shifted into the anodic range of potentials.

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[2] Hence for applied potentials more anodic than 3.0 it is not easy to designate which reaction distribution is most uniform, and arbitrary criteria must be used.

If both cathodic and anodic reactants had been available in unlimited quantity, the reaction distribution would have been most uniform at vanishingly small currents. This behavior is not predicted by simpler models which assume either constant concentration (thus neglecting concentration polarization of the back reaction) or a Tafel kinetic expression (neglecting the back reaction altogether).

The variation of electrode overpotential upon dissolution is shown in Fig. 2. Results are shown for several values of the applied current density, β. The total overpotential of the electrode (the potential in the electrolytic solution at the pore entrance) increases with applied current density.[3] It can be seen that the polarization decreases below the "steady state" value (dashed lines in Fig. 2) and that the decrease in potential sets in earlier for the higher currents.

For the system at hand the theoretical model predicts that the uniformity of the reaction distribution near the pore entrance passes through a maximum at anodic potentials because of the mass transfer limitation of the back reaction as discussed above. Since the porosity distribution is equivalent to the time average current distribution, the "most uniform" final porosity distribution will correspond to a particular anodic current. Currents different from this particular one should lead to porosity distributions which are more nonuniform near the pore entrance. Final porosity distributions are given in Fig. 3 for several applied current densities. The total amount of charge passed is the same for all curves, and thus it may be seen that the model

[3]Although the figure does not illustrate it, one may realize that for the same applied current density, the more rapid reactions, having higher values of ξ, suffer lesser polarization. For the slow reactions, charge transfer overpotential near the pore entrance forces the current deeper into the pore so that the reaction is more uniformly distributed at the expense of higher overpotential.

predicts the most nonuniform reaction distribution at the lowest applied current density (β=18.5). As the applied current density is increased and the duration of electrolysis is decreased, the predicted final porosity distribution becomes more uniform. As the applied current density is increased still further, above β = 148, the porosity distribution near the entrance again begins to become nonuniform.

As dissolution proceeds, the current distribution becomes more uniform since the increased porosity facilitates penetration of current into the pores. Therefore the effect of porosity variation is to render the time average current distribution more uniform than the steady state distribution at uniform (initial) porosity. Also, for the system under study, the induced convection due to volumetric changes upon dissolution tends to make the current distribution more uniform although, for this system, the current distribution is affected by less than 1% over the range of parameters presented here. It is possible that the pseudo-steady state approximation would not be valid for cases where the induced convection was really significant. Although the current distribution thus changes as dissolution proceeds, if the change is only slight, the final porosity distribution may be estimated from the current distribution prevailing at the initial steady state conditions. When the final porosity distribution calculated by the pseudo-steady state model (Fig. 3) were compared with similar results obtained with use of the initial steady state current distribution, the two methods gave results which agreed within 2% for the lower current densities. For β values of 148 and 296, the steady state model predicted porosities near the pore entrance which were up to 10% higher than the pseudo-steady state model.

Conclusions

The performance of dissolving porous electrodes predicted in this work is, of course, subject to the limitations associated with the pseudo-steady state macroscopic model used. The calculated results of the changing electrode structure are all entirely consistent in pattern with what should be expected on the basis of qualitative reasoning.

An interesting aspect of the behavior of anodically dissolving porous systems, although one not directly connected with matrix changes, is also evident in these results. That is the occurrence of the most uniform current distribution within the flooded porous electrode at a particular, non-vanishing applied current density as the result of mass transport limitations on the local cathodic (back) reaction.

In most practical flooded electrodes local variations in overpotential behavior due to inhomogeneities in the solid state, changes in microscopic configuration in the course of electrode reaction, and effects from reaction at the external electrode surface may cause significant deviations from the behavior patterns predicted by this theory. Also, in many systems, products, as well as reactants, appear in the solid state. However, consideration of these more complex cases will require better knowledge of mechanisms of electrode reactions and of the composition and distribution of solid materials in such electrodes before any meaningful quantitative analysis can be undertaken. In the meantime, useful insight into several performance characteristics for flooded porous electrodes can be gained from the present simplified theory. The pseudo-steady state approach can be extended to more realistic cases as necessary information becomes available.

Acknowledgment

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NOTATION

A	a/a_o, cross sectional area of electrolyte, dimensionless.
a	cross sectional sectional area of electrolyte, cm^2.
C_i	c_i/c_{ref}, concentration of species i, dimensionless.
c_i	concentration of species i, $gmol/cm^3$.
c_{ref}	reference concentration, $gmol/cm^3$.
D_i	diffusion coefficient of species i, cm^2/s
D_{ref}	reference diffusion coefficient, cm^2/s
d	thickness of electrode, cm.
e	symbol for electronic charge.
F	Faraday's constant, 96,500 coul/gm-equiv.
I	i/i^*, current density in the electrolyte, dimensionless.
i	current density in the electrolyte, A/cm^2.
i^*	current density in the electrolyte at the pore mouth, A/cm^2.
i_o	exchange current density of the reaction rate expression, A/cm^2.
J	$\ell dj/i^*a_f$, transfer current density, dimensionless.
j	transfer current density, A/cm^2.
L	ℓ/ℓ_o, perimeter of pore, dimensionless.
ℓ	perimeter of pore, cm.
M_i	symbol for specie i taking part in electrode reaction.
m_i	molecular weight of species i
N_i	flux of species i, $gmol/cm^2s$
n	number of electrons taking part in reaction according to Eq. (5).
P	porosity of electrode.
R	gas constant, joules/gmol °K
r	equivalent pore radius, cm.

S_i source term for species i, gmol/cm^{3}s

T temperature, °K

t time, s

$\bar{V}$ specific volume of electrode metal, cm^3/gmol.

v mass average fluid velocity, cm/s

Y y/ℓ, spatial variable in one-dimensional model, dimensionless.

y spatial variable in one-dimensional model, cm.

z_i charge number of ionic species i.

Greek Letters

α_a anodic transfer coefficient in reaction rate expression.

α_c cathodic transfer coefficient in reaction rate expression.

β $i^*a_f d/nFc_{ref}D_{ref}a_o$, dimensionless applied current density parameter.

γ_i c_i/c_{ref}, bulk concentration of species i, dimensionless.

ρ_m density of metal, gm/cm^3.

ρ_s density of electrolytic, solution, gm/cm^3.

ζ $i^*a_f\bar{V}_m d/nFD_{ref}a_o$, dimensionless velocity parameter.

ν_i stoichiometric coefficient of species i according to Eq. (5).

ξ $i_o d^2\ell_o/nFc_{ref}D_{ref}a_o$, dimensionless kinetic parameter

π_i D_i/D_{ref}, diffusion coefficient of species i, dimensionless.

Φ $F(\phi-\phi_e)/RT$, polarization, dimensionless.

ϕ electrode potential, V.

ϕ_e equilibrium electrode potential, V.

τ $\bar{V}i^*a_f t/nFd$, time, dimensionless.

Subscripts

f value at entrance of pore, $y = d$.

i species i.

o initial value at onset of dissolution.

Superscripts

' derivative with respect to spatial variable y.

∞ value of variable in bulk electrolytic solution external to the porous electrode.

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Table I. Parameters for porous copper anode system

$\rho_m = 8.94\ gm/cm^3$	$n = 2$
$\rho_s = 1.00\ gm/cm^3$	$\alpha_a = 0.5$
$m_m = 63.54\ gm/gmol$	$\alpha_c = 0.5$
$a_o = 1.964 \times 10^{-5} cm^2$	$c_{ref} = 10^{-3} gmol/cm^3$
$\ell_o = 2.22 \times 10^{-2} cm$	$D_{ref} = 10^{-5} cm^2/s$
$d = 0.5\ cm$	
$P_o = 0.035$	

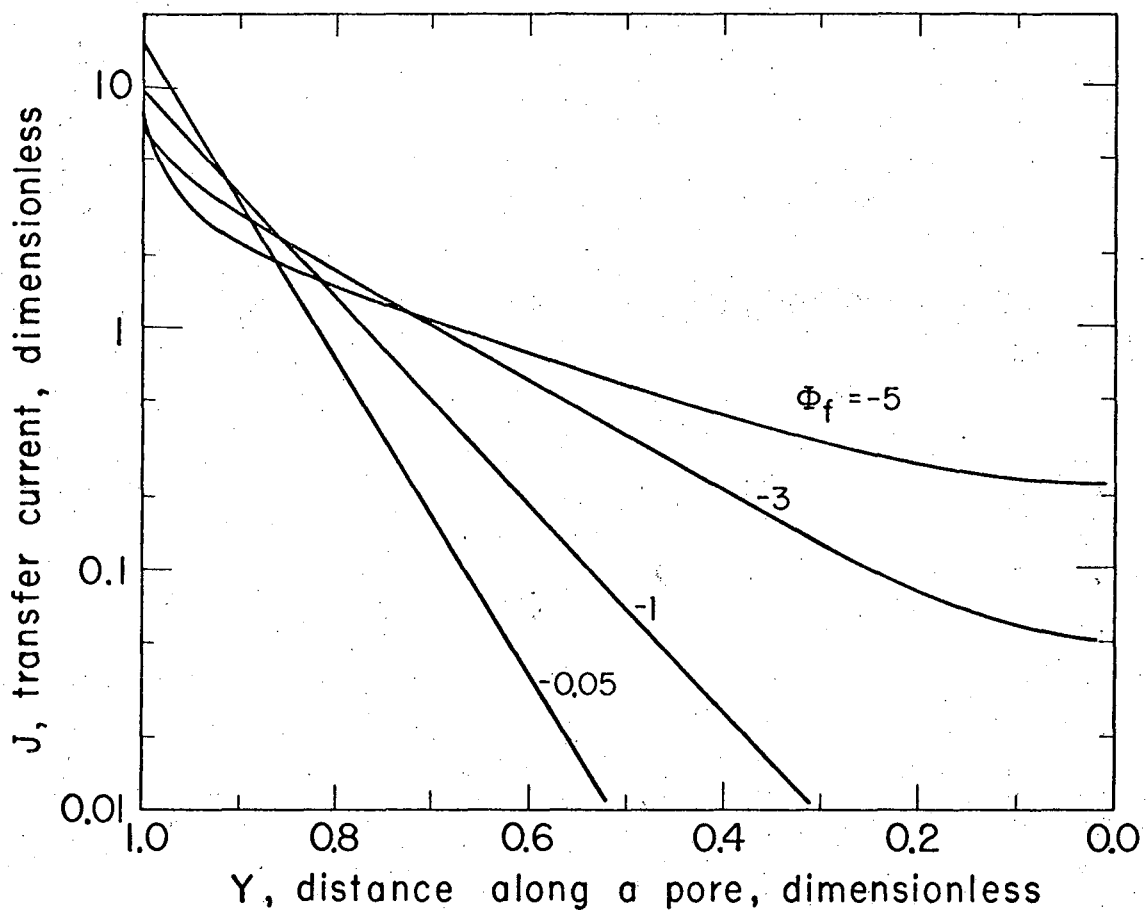
$\nu_1 = -1$	$\nu_2 = 0$	$\nu_3 = 0$
$z_1 = +2$	$z_2 = -1$	$z_3 = +1$
$\gamma_1 = 0.145$	$\gamma_2 = 2.33$	$\gamma_3 = 2.04$
$\pi_1 = 0.7188$	$\pi_2 = 1.331$	$\pi_3 = 9.312$

FIGURE CAPTIONS

Fig. 1. Steady state current distribution in porous copper anode for $\xi = 25$ at several electrode overpotentials (Φ_f).

Fig. 2. Potential variation during dissolution of porous copper anode for $\xi = 400$ at several applied current densities (β).

Fig. 3. Porosity distribution for porous copper anode after dissolution for 0.05 A-hr at several current densities (ξ=400).



XBL6810 - 7095

Fig. 1

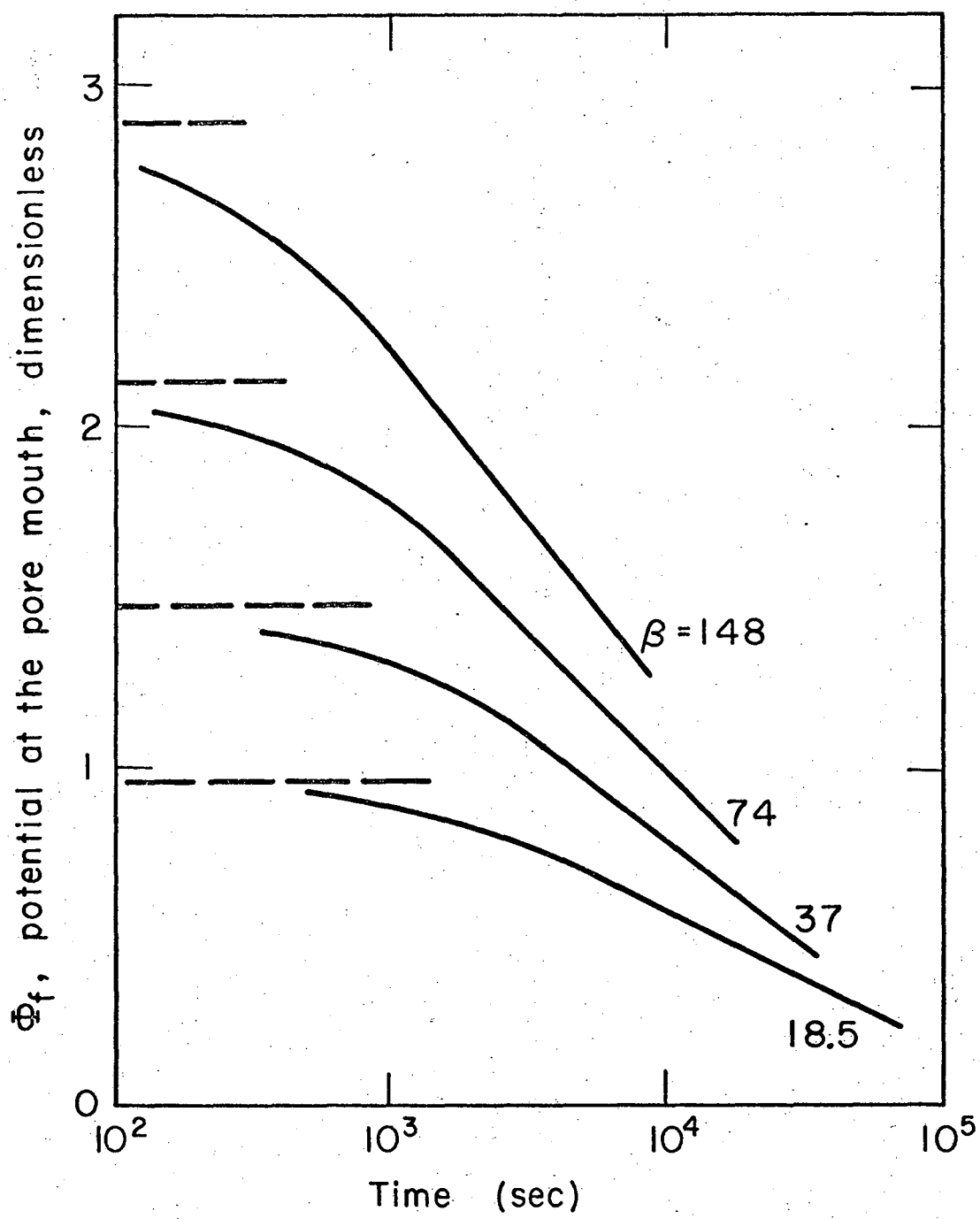


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Fig. 2

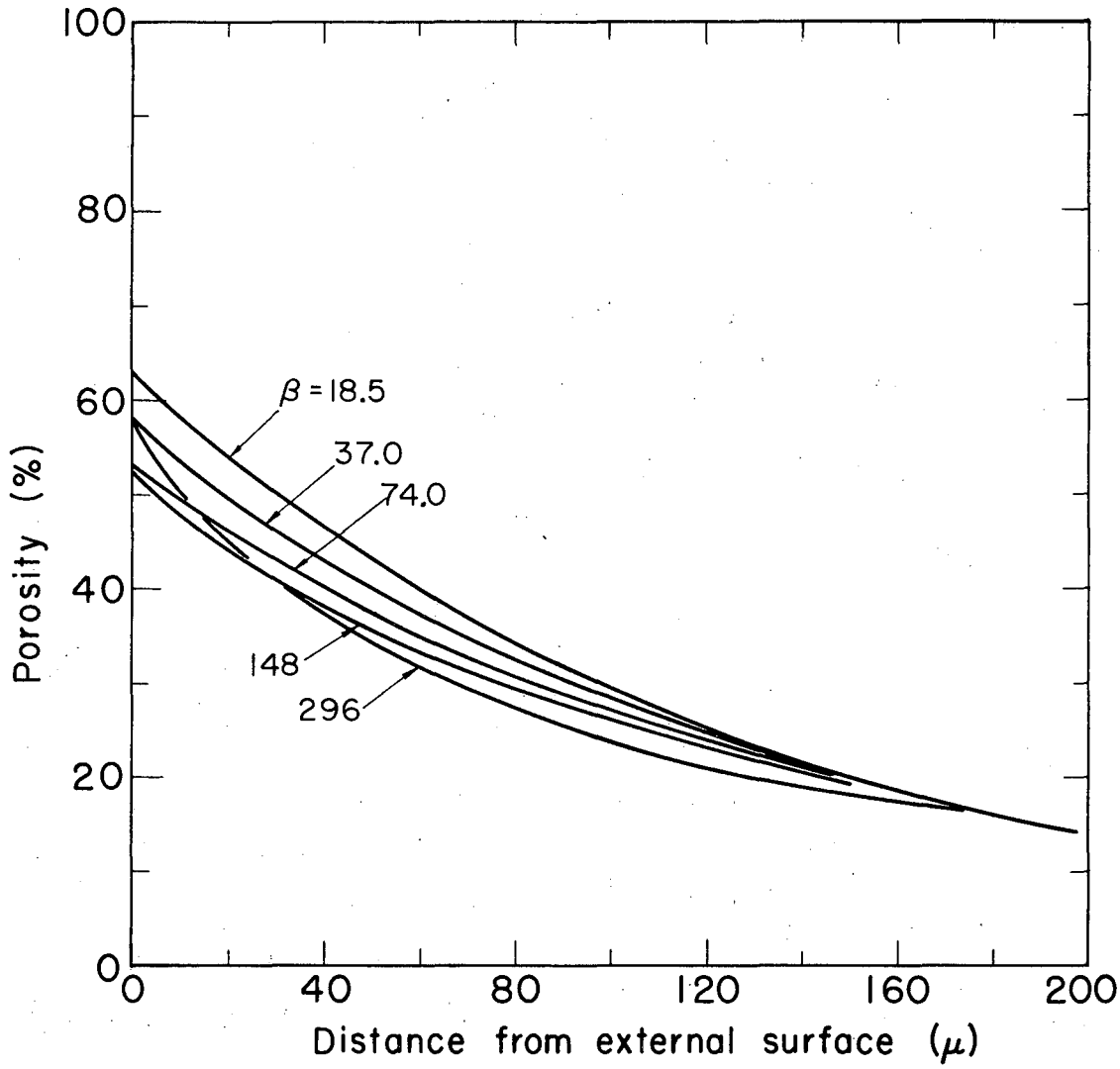

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Fig. 3

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