Lawrence Berkeley National Laboratory

Recent Work

Title

TRANSIENT BEHAVIOUR OF POROUS ELECTRODES WITH HIGH EXCHANGE CURRENT DENSITIES

Permalink

<https://escholarship.org/uc/item/79m0k91s>

Author

Pollard, Richard

Publication Date

1978-10-01

TRANSIENT BEHAVIOUR OF POROUS ELECTRODES WITH HIGH
EXCHANGE CURRENT DENSITIES

Richard Pollard and John Newman

RECEIVED
LAWRENCE
BERKELEY LABORATORY

October 1978

JAN 19 1979

LIBRARY AND
DOCUMENTS SECTION

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782

LBL-8317
c-2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Transient Behaviour of Porous Electrodes with High Exchange Current Densities

Richard Pollard and John Newman

Materials and Molecular Research Division, Lawrence Berkeley Laboratory
and Department of Chemical Engineering, University of California,
Berkeley, California 94720

October 1978

Abstract

A theoretical analysis of the non-steady state reaction distribution in a porous electrode with a high exchange current density is made by application of a simplified macrohomogeneous model for porous electrodes. The dimensionless transfer current for short times is given as an expansion in time, and two terms in a moderate time solution are also presented. At moderate times the current is split into time-dependent and time-independent parts, but this distinction is not apparent in the short time solution. For the limiting case of reversible kinetics, the analysis specifies the fraction of the superficial current density that will be distributed through the electrode. Treatments for the PbO_2 and LiAl electrodes are presented as examples.

Introduction

Many porous electrodes in commercially important batteries have high values for the product of the electrochemically active specific interfacial area and the exchange current density. This permits operation at high superficial current densities without excessive surface overpotentials that would lower the energy efficiency of the system.

Previously, the distributions of current and electrochemical reaction in porous electrodes have been considered under various special conditions [1,2]. Mass transport of reactants and the effective conductivities of the matrix and solution phases have a strong influence on electrode behaviour. The current distribution becomes non-uniform for large values of active surface area, exchange current density, electrode length, and current density and for small conductivities.

Particular attention has been paid to the electrodes of the lead-acid battery [3,4], and several of the proposed models make the assumption of reversible kinetics [5,6]. With this assumption, it has been shown that, in principle, a fraction of the total reaction will be restricted to the electrode/separator interface [5]. However, the other study allows all the current to penetrate the electrode [6].

This paper considers the nature of the current and reaction distributions for electrode processes with high, but not infinite, exchange current densities. A simplified model is developed in order to give an analytic solution to the governing differential equations.

The results obtained illustrate the important features that would be observed with a more sophisticated approach. The method used in this paper complements a computer solution which is able to account for many complications not considered here, but which cannot easily clarify the highly non-uniform reaction distribution at moderately short times that results from a high value of the exchange current density.

Analysis

The system considered is a porous electrode in contact with an inert porous separator. The electrode is treated as two superposed continua which represent the solution and matrix phases independently. The actual geometric details of the pores have been disregarded and only variations of parameters in a direction normal to the electrode face are considered. Each phase is taken to be electrically neutral, and consequently the divergence of the total current density is zero.

The analysis is restricted to a single electrode reaction with stoichiometry represented by:

A polarisation equation of the form

$$j = ai_o \left[e^{\alpha_a F(\Phi_1 - \Phi_2)/RT} - e^{-\alpha_c F(\Phi_1 - \Phi_2)/RT} \right] \quad (2)$$

is used to express the dependence of the local reaction rate on the potential jump at the matrix solution interface. The potential of the pore solution Φ_2 is measured with a reference electrode of the same kind as the working electrode. The composition dependence of the exchange current density is assumed to have the form:

$$i_o = i_{oR} \prod_i \left(\frac{c_i}{c_{iR}} \right)^{\gamma_i} \quad (3)$$

where i ranges over the ionic species. Solid phase activities are taken as constant, and initial concentrations are used for the reference condition, R . The possibility of homogeneous chemical reactions is not considered, and double layer charging effects are ignored. To simplify the analysis further, it is assumed that transport properties and pore structure do not change as the reaction proceeds. Under these circumstances, the major concentration changes are caused by electrochemical reaction and by diffusion of electrolyte. Therefore, a non-steady state material balance for species i becomes:

$$\epsilon \frac{\partial c_i}{\partial t} = \frac{B}{F} j + \epsilon D \frac{\partial^2 c_i}{\partial y^2} \quad (4)$$

For times over which equation (4) is to be applied, the parameter B is taken as a constant, dependent on the system considered. Relationships for B , for the positive plate of a lead-acid battery and for the negative electrode in a high temperature LiAl/LiCl , KCl/FeS_x battery, are derived in Appendices I and II, respectively. The molecular diffusion coefficient D can be characterised by

$$D = D_{\infty} / \zeta^2 . \quad (5)$$

Also, it is assumed that the tortuosity factor ζ is directly related to porosity by [7]:

$$\zeta = \varepsilon^{(1-q)/2} \quad (6)$$

where the constant q is taken as 1.5.

The driving force for the current can be specified in terms of the potential in the pore solution Φ_2 measured with a reference electrode. With this definition, a modified Ohm's law for the pore electrolyte is

$$\frac{i_2}{\kappa} = -\nabla \Phi_2 + \frac{RT}{F} W \nabla \ln c_i \quad (7)$$

where the second term on the right includes the diffusion potential. In this analysis, the parameter W is regarded as a constant, dependent on the electrode studied (see Appendices I and II). The effective conductivity κ is estimated from

$$\kappa = \varepsilon \kappa_{\infty} / \zeta^2 , \quad (8)$$

together with equation (6).

The movement of electrons in the matrix phase is governed by Ohm's law. However, it is assumed that the matrix conductivity is large ($\sigma/\kappa \gg 1$) so that the matrix potential can be taken to be uniform. With this condition, the initial electrode reaction will be

confined to a region adjacent to the electrode/separator interface. This reaction zone can be characterised with a penetration depth L which, for linear kinetics and constant matrix potential, is defined as [8]:

$$L = \left(\frac{\kappa RT}{(\alpha_a + \alpha_c) a_{i_o} F} \right)^{1/2} \quad (9)$$

At high values of the exchange current density or the product a_{i_o} , the local surface overpotential for a specified superficial current density I is expected to be low. Therefore, it is reasonable to reduce equation (2) to linear kinetics in the form

$$\frac{J}{\eta} = \prod_i \left(1 + \frac{IL\theta}{\epsilon D F c_i^o} \right)^{\gamma_i} \quad (10)$$

where $J = jL/I$, $\eta = \kappa(\Phi_1 - \Phi_2)/IL$, and $\theta = F\epsilon D(c_i - c_i^o)/IL$. The penetration depth L is very small at high exchange current densities, and one may simplify Eq. (10) further to obtain:

$$J = \eta \quad (11)$$

Also, it becomes valid to linearise the concentration dependent term in Eq. (7). Combination of Eqs. (7) and (11) then gives, on differentiation:

$$J = \frac{d^2 J}{dY^2} + Q \frac{d^2 \theta}{dY^2} \quad (12)$$

where $Y = y/L$ and

$$Q = \frac{\kappa_{\infty} RT BW}{D_{\infty} c_i^0 F^2} . \quad (13)$$

The material balance, Eq. (4), can be rewritten in dimensionless form

$$\frac{\partial \theta}{\partial \tau} = J + \frac{\partial^2 \theta}{\partial Y^2} \quad (14)$$

where $\tau = Dt/L^2$.

The governing differential equations, (12) and (14), are subject to the initial condition

$$\theta(Y, 0) = 0 , \quad (15)$$

and the boundary conditions

- (i) $\theta(Y, \tau) \rightarrow 0$ as $Y \rightarrow \infty$,
- (ii) at the electrode/seperator interface ($Y = 0$);
 - a) $i_2 = -I$,
 - b) θ continuous,
 - c) $\left(\epsilon D \frac{\partial \theta}{\partial Y} \right)_{os} = \left(\epsilon D \frac{\partial \theta}{\partial Y} \right)_{oe}$.

(16)

For condition (i), the electrode is assumed to be considerably thicker than the penetration depth so that its length can be regarded as infinite. The last boundary condition assumes that the reaction rate is not a Dirac δ function at the origin.

Equations (12) to (16) define the dependence of concentration and transfer current on time and distance through the porous electrode for a constant current discharge. The reaction zone is restricted to the region immediately adjacent to the separator, and this limits the applicability of the results, as discussed below. The equations refer to systems with high exchange current densities or small penetration depths, but it should be emphasised that the macro-homogeneous model on which the analysis is based will breakdown if the reaction zone is significantly smaller than the characteristic dimensions of the microscopic porous structure.

Results and Discussion

In terms of Laplace transforms, the solution to the stated problem may be written as:

$$\bar{J}(Y,s) = Ae^{-EY} + \frac{1}{E\sqrt{s}} \left(1 - \frac{As}{E}\right) e^{-Y\sqrt{s}/E}, \quad (17)$$

where the variable s is defined by:

$$f(s) = \int_0^{\infty} e^{-s\tau} F(\tau) d\tau. \quad (18)$$

The parameters A and E are related by the imposed requirement that integration of Eq. (17) across the electrode gives the superficial current density, viz:

$$\int_0^{\infty} \bar{J}(Y, s) dY = \frac{1}{s} . \quad (19)$$

Equations (5), (6), (15), (16), and (19) may be combined to specify the coefficient A and E as

$$A = -\frac{1}{s} \left[\frac{(1 - E^2)(1 + P\sqrt{s}/E)}{(1 - s/E^2)(1 + PE)} - 1 \right]^{-1} , \quad (20)$$

and

$$E = \left(\frac{2s}{1 + s + Q + [(1 + s + Q)^2 - 4s]^{1/2}} \right)^{1/2} \quad (21)$$

where

$$P = (\epsilon_s/\epsilon)^{2.5(q-1)} . \quad (22)$$

Equation (18), together with the definitions of τ and L , indicates that the variable s is inversely proportional to the exchange current density. Consequently, inversion of Eq. (17) in the limit as $s \rightarrow 0$ should give a moderate time solution for the dimensionless transfer current. Two terms in the inverse Laplace transform for Eq. (17) are

$$J = \sqrt{1+Q} \lambda e^{-\sqrt{1+Q} Y} + \frac{1-\lambda}{\sqrt{\pi(1+Q)\tau}} e^{-\eta^2} . \quad (23)$$

where

$$\lambda = \frac{P\sqrt{1+Q} + 1}{P\sqrt{1+Q} + 1 + Q} \quad (24)$$

and

$$\eta = Y/2\sqrt{(1+Q)\tau} . \quad (25)$$

The variables Y and η can be regarded as inner and outer perturbation parameters, respectively. In the region $Y \lesssim 0(1)$, Eq. (23) describes the reaction zone immediately adjacent to the separator, whereas in the region $\eta \gtrsim 0(1)$ it describes the progressive penetration of the reaction through the electrode. The first term in the equation represents a time-independent spike in J which is largest at the separator and which penetrates a relatively short distance into the electrode. The factor $\sqrt{1+Q}$ in the exponent reflects the influence of diffusion on the spike shape.

The fraction of the total current associated with the spike, λ , is an important parameter in the description of an electrode process with a high exchange current density. If λ is small, most of the current will be progressively distributed through the electrode whereas, as λ approaches unity, it becomes more acceptable to disregard the time-dependent term in equation (23) and to assume that the reaction is restricted to the spike alone. The spike is sharper for larger exchange current densities, and in the limit of infinite exchange current density it will become a Dirac δ function (with area λI) at the electrode/separator interface. Consequently, in electrode models that neglect the surface overpotential (reversible kinetics, $i_0 = \infty$), only a fraction $(1 - \lambda)$ of the total current should be distributed through the electrode.

Two examples have been chosen to illustrate these concepts; the positive plate of a lead-acid battery and the negative electrode of a LiAl/FeS_x high temperature cell with molten LiCl , KCl electrolyte. For the lead-acid system, it is assumed that the electrolyte dissociates completely. The reaction for discharge of the lead dioxide electrode is then

The stoichiometric coefficients defined in accordance with Eq. (1) are, $s_+ = -2$, $s_- = -\frac{1}{2}$, $s_0 = 1$, and $n = 1$. With the electrode parameters given in Table 1, the model proposed indicates that 39% of the superficial current density is associated with the time-independent spike in Eq. (23).

The reaction at the LiAl electrode of the high temperature battery is

and therefore, $s_+ = -1$, $s_- = 0$, $s_0 = 0$ and $n = 1$. Table 1 lists system parameters for discharge with an electrolyte of eutectic composition. The analysis shows that 85% of the total current is in the spike. Figure 1 gives the dependence of the dimensionless transfer current on the inner perturbation parameter Y for the LiAl electrode. For small values of Y , the major contribution to J is from the time-independent term in Eq. (23), and the distance over which the

Table 1. Typical parameters for PbO_2 and LiAl electrodes

Parameter	PbO_2	LiAl	Parameter
κ_∞ (mho/cm)	0.91	1.75	κ_∞ (mho/cm)
$D_\infty \times 10^5$ (cm^2/s)	3.03	3.33	$D_\infty \times 10^5$ (cm^2/s)
T(K)	298.15	723.15	T(K)
ϵ_s^o	0.56	0.75	ϵ_s^o
ϵ^o	0.52	0.20	ϵ^o
$\alpha_a = \alpha_c$	0.50	0.50	$\alpha_a = \alpha_c$
$10^3 C_e^o$ (mol/ cm^3)	5.00	0.58	x_A^o
ρ (g/ cm^3)	1.29	33.92	$\tilde{V}$ (cm^3/mol)
$1 + \frac{d \ln \gamma}{d \ln m}$	2.30	1.92	$1 + \frac{d \ln \gamma_A}{d \ln x_A}$
t_+^o	0.73	0.29	t_1^*
P	1.10	5.22	P
Q	6.17	1.60	Q
λ	0.39	0.85	λ
L(cm)	0.42	1.32×10^{-3}	L(cm)

XBL7810-6071

Figure 1. Solution in the inner region for the dimensionless transfer current at different times, τ , for the LiAl electrode, as predicted with Eq. (23). The solution at $\tau = 0$ is from Eq. (28).
 ----- time-independent spike.

spike is dominant increases with time for $\tau \gtrsim 10$. At progressively larger times the reaction penetrates further into the electrode, and J falls locally in response to the requirement of constant total current. Eventually the material closest to the separator will become depleted of reactant, and the narrow reaction zone will then move through the electrode as the available material is consumed. At this stage, the analysis presented here will no longer be valid. Additional complications can arise if local changes in composition significantly affect the exchange current density through Eq. (3). For example, if i_0 is most sensitive to the reactant concentration, it is expected that the spike will become more diffuse as the reaction proceeds. This is not accounted for by the model, although concentration changes are included in the non-steady state material balance, Eq. (14).

The zero time solution of Eq. (17),

$$J = e^{-Y}, \quad (28)$$

is also shown in Fig. 1 in order to emphasise how the reaction distribution becomes separated into two components that correspond to the two terms in Eq. (23). The apparent agreement between the zero time solution and the reaction distribution at $\tau = 1$ is coincidental; the moderate time solution cannot be extended to $\tau < 1$ and, moreover, an assessment of the influence of higher order terms not shown in Eq. (23) is needed to establish its validity at $\tau = 1$.

Figure 2 shows the inner solution at moderate times for the PbO_2 electrode. The different values for the parameters Q and λ , in

XBL7810-6072

Figure 2. Solution in the inner region for the dimensionless transfer current at different times, τ , for the PbO_2 electrode, as predicted with Eq. (23). The solution at $\tau = 0$ is from Eq. (28).
 ----- time-independent spike.

comparison with the LiAl electrode, both make the penetration of the spike smaller and hence reduce the contribution of this term to the total transfer current at a given position in the electrode. The penetration depth for the PbO_2 system, as calculated with Eq. (9), is approximately 0.4 cm, which is considerably larger than the corresponding value for the LiAl electrode (see Table 1). For this reason, the results of a high current density analysis for the PbO_2 electrode should be treated with caution and, in particular, the assumption of reversible kinetics that has been used previously [5,6] requires some justification.

The outer solution for J for the LiAl electrode at moderate times is given in Fig. 3 in terms of the outer perturbation parameter, η . The incomplete curves show the contribution of the time-dependent term in Eq. (23). The intercepts of these parabolae represent inner limits of the outer expansion, given by $(1 - \lambda)/\sqrt{\pi(1 + Q)\tau}$. This is also seen in Fig. 1 as the magnitude of J in the region where the current associated with the spike is negligible. The dimensionless distance within which half the current that penetrates is to be found is given by $0.98\sqrt{(1 + Q)\tau}$. This dependence indicates that the process is dominated by diffusion but that interactions between diffusion and reaction modify the current distribution.

The reaction rate distribution at very short times is obtained as a power series expansion in τ , by inversion of Eq. (17) in the limit as $s \rightarrow \infty$. It is found that

XBL 7810-6073

Figure 2. Solution in the inner region for the dimensionless transfer current at different times, τ , for the LiAl electrode, as predicted with Eq. (23). The solution at $\tau = 0$ is from Eq. (28).
 ----- time-dependent term in Eq. (23).

$$\begin{aligned}
 J = e^{-Y} & \left[I_0(\alpha) - \frac{Q\tau}{\alpha} I_1(\alpha) - \frac{2\sqrt{2} PQ}{1+P} \left(\frac{\tau}{\alpha} \right)^{3/2} I_{3/2}(\alpha) \right] \\
 & + \left(\frac{PQ}{1+P} \right) \tau \left[(1 + 2z^2) \operatorname{erfc}(z) - \frac{2z}{\sqrt{\pi}} e^{-z^2} \right] \\
 & + \left(\frac{8Q}{1+P} \right) \tau^{3/2} \left[\frac{(1 + z^2)}{6\sqrt{\pi}} e^{-z^2} - \frac{z}{4} \left(1 + \frac{2z^2}{3} \right) \operatorname{erfc}(z) \right]
 \end{aligned} \tag{29}$$

where $\alpha = \sqrt{2Q\tau Y}$, $z = \sqrt{1+Q} \eta$, and $I_\nu(\alpha)$ is a modified Bessel function of the first kind and of order ν .

For short times, e.g. $\tau < 0(10^{-2})$, J can be predicted adequately by the zero time solution, Eq. (28). At first sight, the e^{-Y} term in Eq. (29) would seem to be equivalent to the spike observed in the moderate time solution. Numerically, however, the clear distinction between the two contributions at moderate times has not developed at the short times for which Eq. (29) is valid. This range of validity can be assessed by a comparison of the first order, short-time approximation for J with the approximations accurate to orders τ and $\tau^{3/2}$ (J_1 , J_2 , J_3 respectively). Figure 4 shows that, for the LiAl electrode, the validity of Eq. (29) becomes questionable for $\tau > 0.1$. At $\tau = 0.1$, inclusion of the $\tau^{3/2}$ term causes a relatively minor shift in J_2 . At $\tau = 0.5$, the difference between J_2 and J_3 indicates that higher order terms are needed to obtain a satisfactory solution. For the PbO_2 electrode, the range of validity of Eq. (29) is restricted to even smaller values for τ because the parameter Q is significantly larger than for the LiAl system (see Table 1).

XBL7810-6074

Figure 4. Reaction rate distribution for LiAl electrode at short times, as predicted with Eq. (29). J_1 , J_2 , J_3 , are first, second, and third order approximations, respectively.

The distinct differences in short and moderate time behaviour predicted by equations (23) and (29) preclude the formation of a combined perturbation expansion that would provide an acceptable link between the two time regions. A more general inversion of the solution in Laplace space, Eq. (17), is needed to be able to predict this intermediate behaviour.

Conclusions

A simplified macrohomogeneous model can be used to elucidate the transient behaviour of porous electrodes with high exchange current densities. The highly non-uniform initial reaction distribution changes at moderately short times due to the influence of concentration overpotential.

Acknowledgement

This work was supported by the Division of Solar, Geothermal, Electric and Storage Systems, Office of the Assistant Secretary for Energy Technology, U.S. Department of Energy.

Nomenclature

a	interfacial area per unit electrode volume (cm^{-1})
A	variable in s domain defined by Eq. (20)
B	parameter in Eq. (4)
c_i	concentration of species i (mol/cm^3)
c_T	total ionic concentration (mol/cm^3)
D	molecular diffusion coefficient of pore electrolyte (cm^2/s)
E	variable in s domain defined by Eq. (21)
F	Faraday's constant (96487 C/equiv)
G	parameter defined by Eq. (39)
i_o	exchange current density (A/cm^2)
$\underline{i}_2$	superficial current density in pore phase (A/cm^2)
I	superficial current density to an electrode (A/cm^2)
j	$= \nabla \cdot \underline{i}_2$, transfer current per unit electrode volume (A/cm^3)
J	dimensionless transfer current
$\bar{J}$	dimensionless transfer current in s domain
L	penetration depth (cm)
m	molality of electrolyte (mol/kg)
M_i	symbol for the chemical formula of species i
n	number of electrons transferred in electrode reaction
$\underline{N}_i$	superficial flux of species i ($\text{mol}/\text{cm}^2 \cdot \text{s}$)
P	parameter defined by Eq. (22)
q	parameter defined by Eq. (6)
Q	parameter defined by Eq. (13)
R	universal gas constant (8.3143 J/mol.K)

s	variable defined by Eq. (18)
s_i	stoichiometric coefficient of species i in electrode reaction
t	time(s)
t_i^o	transference number of species i relative to solvent velocity
t_i^c	transference number of species i relative to common ion velocity
$t_i^\star$	transference number of species i relative to molar average velocity
T	absolute temperature (K)
$v^\star$	molar average velocity (cm^2/s)
$v^\square$	superficial volume average velocity (cm^2/s)
$\bar{V}_i$	partial molar volume of species i (cm^3/mol)
$\tilde{V}$	molar volume of electrolyte (cm^3/mol)
W	parameter defined by Eq. (7)
x_A	mole fraction of salt A
y	distance through electrode measured from separator (cm)
Y	dimensionless distance through porous electrode measured from separator
z_i	valence or charge number of species i
Greek letters	
α_a	transfer coefficient in anodic direction
α_c	transfer coefficient in cathodic direction
γ	mean molal activity coefficient
γ_i	exponent in Eq. (3)
γ_A	activity coefficient for salt A
ϵ	porosity or void volume fraction
ζ	tortuosity defined by Eq. (6)
η	outer perturbation parameter defined by Eq. (25)

η	dimensionless surface overpotential
θ	dimensionless concentration
κ	effective solution conductivity (mho/cm)
λ	parameter defined by Eq. (24)
μ_e	chemical potential of electrolyte (J/mol)
μ_A	chemical potential of salt A (J/mol)
ν	total number of ions produced by dissociation of a mole of electrolyte
ν_i	number of moles of species i produced by dissociation of a mole of electrolyte
ρ	density of electrolyte (g/cm ³)
σ	effective matrix conductivity (mho/cm)
τ	dimensionless time
Φ_1	electric potential in the matrix (V)
Φ_2	electric potential in the solution (V)

Subscripts

A	lithium chloride
B	potassium chloride
e	electrolyte
o	solvent
os	in separator at electrode/separator boundary
oe	in electrode at electrode/separator boundary
R	reference condition
∞	bulk solution property

Superscripts

- A lithium chloride
- B potassium chloride
- o initial value

References

1. J. Newman and C. W. Tobias, J. Electrochem. Soc., 109, 1183 (1962).
2. J. Newman, Internal tech. report, NOLC project, Dept. of Chem. Eng., Univ. of California, Berkeley (1962).
3. K. Micka and I. Rousar, Electrochim. Acta, 21, 599 (1976).
4. D. Simonsson, J. Appl. Electrochem., 3, 261 (1973).
5. W. Stein, Ph.D. thesis, Rheinisch-Westfalischen Techn. Hochschule, Aachen (1959).
6. K. Micka and I. Rousar, Electrochim. Acta, 18, 629 (1973).
7. J. Newman and W. Tiedemann, "Advances in Electrochemistry and Electrochemical Engineering," Vol. 11, H. Gerischer and C. W. Tobias, Editors, Wiley-Interscience, (1977).
8. J. Newman and W. Tiedemann, A.I.Ch.E. Journal, 21, 25 (1975).
9. J. Newman and T. W. Chapman, A.I.Ch.E. Journal, 19, 343 (1973).
10. R. Pollard and J. Newman, submitted for publication.
11. M. Blander in "Molten Salt Chemistry," M. Blander, Editor, pp. 127-238, Interscience (1964).

Appendices

Derivation of Parameters for Porous Electrode Model

Appendix I. Positive Plate of Lead-Acid Battery

In the PbO_2 electrode, a non-steady state material balance for species i may be combined with Faraday's law to give

$$\frac{\partial(\epsilon c_i)}{\partial t} = -\nabla \cdot \underline{N}_i - \frac{s_i}{nF} j \quad (30)$$

for a single electrode reaction [8]. For a concentrated binary electrolyte, the superficial flux of species i can be expressed in terms of the superficial volume average velocity $\underline{v}$ [8,9],

$$\underline{N}_i = -\epsilon D \nabla c_i + \frac{t_i^o}{z_i F} i_2 + c_i \underline{v} \quad (31)$$

Substitution into Eq. (30) and comparison with Eq. (4) defines the parameter B as

$$B = \frac{v_i c_o \bar{V}_o}{n} \left[\frac{s_o c}{c_o} - \left(\frac{s_+ t_-^o}{v_+} + \frac{s_- t_+^o}{v_-} \right) \right] \quad (32)$$

Ohm's law can be used in the form

$$\frac{i_2}{\kappa} = -\nabla \phi_2 + \frac{B}{v_i c_o \bar{V}_o F} \nabla \mu_e \quad (33)$$

where Φ_2 is the potential in the pore solution measured with a reference electrode of the same kind as the working electrode. The chemical potential of the electrolyte can be defined with

$$\nabla \mu_e = \frac{vRT}{c_o \bar{v}_o} \left(1 + \frac{d \ln \gamma}{d \ln m} \right) \nabla \ln c_i \quad (34)$$

where v is the total number of cations and anions produced by dissociation of one molecule. Consequently, the parameter W in Eq. (7) is given by

$$W = \frac{vB}{v_i (c_o \bar{v}_o)^2} \left(1 + \frac{d \ln \gamma}{d \ln m} \right). \quad (35)$$

Appendix II. Negative Electrode of LiAl/FeS_x Battery

This high temperature system can use an electrolyte that comprises two binary molten salts with a common ion, such as the LiCl, KCl eutectic. In the derivation below, subscripts 1, 2, and 3 refer to Li^+ , K^+ , and Cl^- ions, respectively, and scripts A and B refer, in turn, to the LiCl and KCl salts. The superficial flux of lithium ions based on the molar average reference velocity is [10]

$$\bar{N}_1 = - \frac{\varepsilon (c_A + c_B)^2 D v_1^A v_1^B}{c_T} \nabla x_A + \frac{t_{1-2}^*}{z_1 F} + c_1 v_1^*, \quad (36)$$

where $x_A = c_A / (c_A + c_B)$ is the mole fraction of LiCl in the electrolyte and c_T is the total concentration defined by $c_T = c_1 + c_2 + c_3$.

Combination of Eqs. (30) and (36) gives, on simplification, Eq. (4)

with

$$B = \tilde{V} \left[\frac{c_A}{v_2^B} \left(\frac{s_2}{n} + \frac{t_2^*}{z_2} \right) - \frac{c_B}{v_1^A} \left(\frac{s_1}{n} + \frac{t_1^*}{z_1} \right) \right], \quad (37)$$

provided that the molar volume of electrolyte $\tilde{V}$ is constant. Ohm's law for the pore electrolyte can be written in a form analogous to Eq. (33) as

$$\frac{i_2}{K} = -\nabla \phi_2 - \frac{G}{F} \nabla \mu_A \quad (38)$$

where

$$G = \left(\frac{s_1}{n v_1^A} + \frac{t_1^c}{z_1 v_1^A} \right) \left(1 + \frac{v_3^A c_A}{v_3^B c_B} \right) - \frac{s_3 c_A}{n c_B v_3^B}. \quad (39)$$

The activity coefficient of a salt in a binary molten salt electrolyte mixture is often defined without regard for dissociation and in terms of ion equivalent fractions or mole fractions [11].

(These composition variables are equivalent when $v_3^A = v_3^B$.) The gradient of chemical potential can be written as [10]

$$\nabla \mu_A = RT \left(v_1^A + \frac{d \ln \gamma_A}{d \ln x_A} \right) \nabla \ln c_A, \quad (40)$$

and with this definition the parameter W in Eq. (7) becomes

$$W = -G \left(v_1^A + \frac{d \ln \gamma_A}{d \ln x_A} \right) . \quad (41)$$

In the absence of experimental data for transference numbers it is assumed that transference numbers are directly proportional to the electrolyte mole fraction, viz: $t_1^\star = v_3^A x_A / v^A$, $t_2^\star = v_3^B x_B / v^B$, and $t_1^c = x_A$.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720