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Abstract

Ion conduction is considered through electrolytes containing an immobile gradient in the electronic/ionic transport number ratio. It is shown that internal deposition of the metal phase (reduced ions) can occur in such electrolytes during electrolysis. A "critical" applied voltage or current density can be formulated above which electrolyte fracture would be caused by the internally deposited material. Application of the analysis to the sodium-beta alumina type electrolytes leads to identification of factors that could contribute to electrolyte degradation.

I. Introduction

Electrochemically induced degradation has been observed in many electrolytes. Stabilized zirconia is an example where at sufficiently high current densities complete reduction with the formation of zirconium metal has been observed [1]. In sodium-beta and beta" electrolytes electrochemical degradation phenomena also occur that lead either to sodium dendrite growth from the negative interface (Mode I) [2-6] or to internal sodium formation (Mode II) [7]. In other materials the electric current may only produce donor ionization or electron-acceptor recombination [8]. Then a steady state is achieved only when the reduction (or oxidation) process has propagated between the electrodes until the entire sample is homogeneous. In this case, the donor or acceptor/electron equilibrium dominates the electronic conductivity. It is, however, possible to conceive of a situation in which recombination reactions, i.e. internal electrolysis, could be driven by the current without a concurrent significant adjustment of the local electronic conductivity. This would be the case if the solid electrolyte were a wide band gap semiconductor in which an immobile gradient in electronic conductivity had been produced by a shallow donor, e.g. by chemical diffusion at high temperature. We consider this here and, following an analysis of Choudhury and Patterson [9], show that at relatively low applied voltages or low current densities, internal electrolysis with formation of the reduced metal phase may be possible. Application of the analysis to Na-beta and -beta'' aluminas gives indications of the limitations on the use of these electrolytes, and provides a different framework for understanding their degradation.

II. Chemical Potential Distribution

Consider a simple ionic solid in which the conduction cations have a charge of +1, giving the equilibrium reaction*

$$M \underset{\Leftarrow}{\overset{\Rightarrow}{}} i + e \tag{1}$$

Transport in such a solid can be described by, Fig. 1,

$$I_i = - \sigma_i \nabla \eta_i / F \tag{2}$$

and

$$I_e = \sigma_e \nabla \eta_e / F \tag{3}$$

provided it is assumed that one particle current is independent of the other's gradient in chemical potential. I_e flows in a direction opposite to I_i. The partial conductivities σ_i and σ_e are defined under Ohmic current flow. Thus, the electrochemical potential gradients of the ions and the electrons, $\nabla \eta_i$ and $\nabla \eta_e$, relate linearly to their respective current densities I_i and I_e. F is Faraday's constant. If the cross-coefficients omitted in Eqs. (2) and (3) are not zero, then the meaning of σ_i and σ_e is more complex. This problem has been treated by Wagner [10], but it will not be considered here. In this paper it will be assumed that σ_i is constant.

_____

* A list of symbols is given at the end of this paper.

This would be expected if the permitted deviations from stoichiometry are small, which is generally the case for ionic crystals. The assumption then simplifies the treatment.

To demonstrate that a steady state can exist, we follow Choudhury and Patterson [9] and define:

$$r = I_i/I_e \qquad (4)$$

so that the total current density $I = I_i + I_e$ from Eq. (2) and (3), becomes:

$$I = \frac{\sigma_i}{F} \frac{(1+r)}{r} (\nabla n_M - \nabla n_e) \qquad (5)$$

r is the parameter that characterizes the steady state. In Eq. (5) we used the relationship $n_M = n_i + n_e$ that follows from Eq. (1) in local equilibrium.

Also, from Eq. (3) and (4) follows that:

$$I = \frac{(1+r)}{F} \sigma_e \nabla n_e \qquad (6)$$

so that from (5) and (6)

$$\nabla n_e = - \frac{\sigma_i}{(r\sigma_e - \sigma_i)} \nabla n_M \qquad (7)$$

Eqs. (3), (6), and (7) permit the evaluation of r. If the average electronic resistivity, R_e, is defined as

$$\bar{R}_e = \frac{1}{\ell} \int_0^\ell \frac{1}{\sigma_e} \, dx \tag{8}$$

then from Eq. (3), and the meaning [9] of the applied electrode potential, V_T,

$$\int_0^\ell \vec{\nabla} \eta_e \, dx \equiv -V_T F = I_e F \ell \, \bar{R}_e \tag{9}$$

or

$$I_e = - V_T (\ell \bar{R}_e)^{-1} \tag{10}$$

From Eqs. (3) and (7) then follows that

$$\int_0^\ell \nabla \eta_M \, dx \equiv \Delta \eta_M^0 = - I_e F \cdot G(\ell, r) \tag{11}$$

where, with σ_i constant,

$$G(\ell, r) = \frac{1}{\sigma_i} \int_0^\ell (r - p^X) \, dx \tag{12}$$

$$\frac{\Delta \eta_M^0}{V_T F} = (\ell \bar{R}_e)^{-1} \cdot G(\ell, r) \tag{13}$$

r follows from evaluation of $G(\ell, r)$ for a specific prescribed spatial dependence of p^X. The expression for r will depend on the nature of p^X. For particular choices of p^X, the expression for r may be very simple. As an example, we chose $p^X = p^C + bx$, where $p^X = \sigma_i / \sigma_e$, and $b = (p^a - p^C)/\ell$, with $p^a \gg p^C$ (p^a is the intrinsic σ_i / σ_e ratio e.g.). Then, from Eq. (13):

$$\int_0^\ell (r - p^X) \, dx \simeq \ell \left(r - \frac{p^a}{2} \right) \tag{14}$$

and

$$r \simeq p^a/2 + \bar{R}_e \sigma_i \Delta\eta_M^0/V_T F \qquad (15)$$

In the present case, the value of r need not be known. This great simplification is actually a consequence of assuming σ_i to be constant.

The conservation of ions anywhere in the sample can be expressed as [9]

$$I_i = -\frac{\sigma_i}{x} \int_0^x \left(\frac{\nabla n_M}{F} - \frac{\nabla n_e}{F}\right) dx \qquad (16)$$

where σ_i is taken to be constant. Since I_i is constant in the steady state one also gets

$$I_i = -\frac{\sigma_i}{\ell} \int_0^\ell \left(\frac{\nabla n_M}{F} - \frac{\nabla n_e}{F}\right) dx \qquad (17)$$

The total applied voltage maintained by the external source, V_T, is, with the same assumptions as Choudhury and Patterson [9]:

$$V_T \equiv -\int_0^\ell \frac{\nabla n_e}{F} dx \ . \qquad (18)$$

or, from Eqn. (3), in the steady state where I_e is independent of x:

$$V_T = -I_e \int_0^\ell \frac{1}{\sigma_e} dx \qquad (19)$$

and defining V_x as

$$V_x = -\int_0^x \frac{\nabla n_e}{F} dx = -I_e \int_0^x \frac{1}{\sigma_e} dx \qquad (20)$$

it then follows from Eqs. (16) and (17) that:

$$\eta_M(x) = \frac{x}{\ell} \Delta n_M^0 + \frac{x}{\ell} V_T F - V_x F \tag{21}$$

V_x can be found from Eqs. (19) and (20):

$$V_x = V_T \left[\int_0^\ell \frac{1}{\sigma_e} \, dx \right]^{-1} \int_0^x \frac{1}{\sigma_e} \, dx \tag{22}$$

Eqn. (21) can thus be written as:

$$\eta_M(x) = \frac{x}{\ell} \Delta n_M^0 + V_T F \cdot f(p^x) \tag{23}$$

where

$$f(p^x) = \frac{x}{\ell} \left(1 - \frac{\frac{1}{x} \int_0^x \frac{1}{\sigma_e} dx}{\frac{1}{\ell} \int_0^\ell \frac{1}{\sigma_e} dx} \right) \tag{24}$$

It can thus be seen that the local value of $\eta_M(x)$ is what it would have been under open circuit conditions modified by a term that depends on the inhomogeneity of the electronic conductivity and on the applied voltage V_T. Eq. (24) shows that the integral ratio in $f(p^x)$ is simply the electronic resistivity averaged between $x = 0$ and $x = x$ divided by the electronic resistivity averaged over the thickness of the electrolyte.

When $\frac{1}{x} \int_0^x \frac{1}{\sigma_e} dx > \frac{1}{\ell} \int_0^\ell \frac{1}{\sigma_e} dx$ then a sufficiently large applied voltage V_T opposed to Δn_M^0, i.e. a charging condition, will give $\eta_M(x) > \frac{x}{\ell} \Delta n_M^0$. $\eta_M(x)$ can in principle reach a positive value meaning M could be formed, under pressure, inside the electrolyte.

If M is considered to be incompressible, a pressure $P(x)$ would be generated equal to $P(x) = n_M(x)/\nu_M$, where ν_M is the molar volume of M. For $n_M/F = 1$ volt a corresponding pressure is 4×10^9 N/M^2 (~570,000 psi). This exceeds the fracture strength of any solid electrolyte by about an order of magnitude.

Since $n_M(x)$ depends on x, we have to find its maximum value, n_M^{max}. n_M^{max} follows readily from putting $\partial n_M(x)/\partial x = 0$. From Eq. (23) one gets that n_M^{max} occurs at $x=x_m$ determined by

$$\nabla[f(p^X)] = -\frac{1}{\ell} \frac{\Delta n_M^0/F}{V_T} \tag{25}$$

To find the value of n_M^{max}, Eq. (25) has to be solved explicitly for x_m so that $f(p^X)$ has to be known or assumed. If, as an example, we assume as before that

$$p^X \equiv \sigma_i/\sigma_e = p^C + x(p^a - p^C)/\ell \tag{26}$$

and make the further simplifying assumption that $p^a \gg p^C$ (plausible when p^a is near the intrinsic value of the wide band gap electronic insulator under consideration), then one finds

$$n_M(x) \simeq \frac{x}{\ell}(\Delta n_M^0 + FV_T) - FV_T \frac{x^2}{\ell^2} \tag{27}$$

and $n_M^{max} = (FV_T + \Delta n_M^0)^2/4FV_T \tag{28}$

at

$$x/\ell = (FV_T + \Delta n_M^0)/2FV_T \tag{29}$$

We could carry the example further, for the sake of illustration, using as a criterion that internal local microfracture due to the electrolysis generated pressure of M would initiate $\eta_M/F \geq 0.1$ volt, when the applied voltage reaches V_T^{crit}. This would correspond to a local internal pressure of about 4×10^8 N/M^2 (~60,000 psi). The internal strength is a materials parameter that depends on the mechanical quality of the electrolyte; a carefully prepared electrolyte might have a higher fracture strength. The value chosen here is fairly representative for polycrystalline electrolytes.

If we define the resistance overvoltage, ΔV, as

$$\Delta V \equiv V_T + \Delta \eta_M^0/F \tag{30}$$

then with Eqn. (28):

$$\Delta V^{crit} \simeq 0.2 + \frac{1}{2}(0.16 + 1.6 |\Delta \eta_M^0|/F)^{1/2} \tag{31}$$

ΔV^{crit} for this particular choice of p^X is sketched in Fig. 2. Consideration of Eqs. (23) and (24) indicates that ΔV^{crit} is sensitive to the choice of p^X. Thus, other forms of p^X should also be considered. Especially the extreme case in which

$$\frac{1}{x}\int_0^X \frac{1}{\sigma_e}\,dx \ll \frac{1}{\ell}\int_0^\ell \frac{1}{\sigma_e}\,dx \text{ in the interval } o < x \leq \delta \text{ and } \sigma_e \text{ is small}$$

and constant in the interval $\delta < x \leq \ell$, may be of interest. This would

correspond to an electrolyte with a significant electronic conductivity in a layer of thickness δ. Then, assuming again that $\eta_M^{(x)}/F$ should not exceed 0.1 Volt, Eq. (23) reduces to $\eta_M(x) = xF\Delta V/\ell$ for $0 < x \leq \delta$ and $\Delta V^{crit} = 0.1\ell/\delta$, since now η_M^{max} occurs at $x = \delta$. An electrolyte in which a partial electronically conductive layer is slowly developing from the negative interface would then be expected to show metal formation and associated micro-cracking at $x = \delta$ for a given applied ΔV, when $\delta = 0.1\ell/\Delta V$.

III. Application of the Analysis to Sodium-Beta Alumina Degradation

Recently De Jonghe et al. [7] reported a slow degradation of sodium-beta alumina solid electrolytes that appeared to take the form of sodium deposition inside the electrolyte with associated micro-cracking. It is thought that the above analysis applies to this type of degradation (Mode II).

When sodium-beta aluminas are in contact with molten sodium they are partly reduced. The process has been found to involve oxygen removal from the electrolyte, leaving oxygen vacancies compensated by electrons. The reduction is accompanied by a discoloration (darkening) of the electrolyte. Detailed experiments clarifying this process have been reported recently by De Jonghe and Buechele [11]. This process of reduction is quite slow, and propagates through the electrolyte at a rate determined by the oxygen vacancy mobility. Increased electronic conductivity associated with the discoloration-reduction process has been reported by Weber [12] and by Desplanches and Wicker [13]. Thus, the chemical action of the sodium produces a quasi-stationary

electronic transport number gradient through the electrolyte. Since
the sodium-beta aluminas are wide band gap insulators [14], it is quite
plausible that the conditions assumed in the previous section are in
fact valid, i.e. $p^a \gg p^c$. In order for the Mode II degradation
to occur by the mechanism proposed here, some gradient in the
electronic transport number should be maintained while the electrolysis
occurs. This requires that the significant change in electronic con-
ductivity establishing p^x, is caused by a slow reaction that differs
from Eq. (1). The slow reaction altering the electronic conductivity
has been identified in our recent work on chemical coloration [11] as:

$$2Na_E + (O_O)_\beta \rightarrow (Na_2O)_E + (V_O^{\cdot\cdot})_\beta + 2(e')_\beta \qquad (32)$$
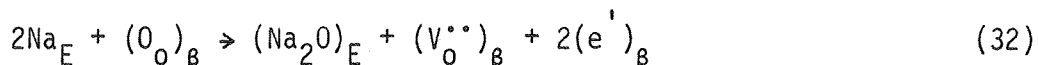
where the Kröger-Vink notation has been used. The subscript β refers
to the sodium-beta or -beta'' alumina, and the subscript E refers to
the electrode. If the reaction described by Eq. (32) would reach
equilibrium very rapidly then Eq. (1) would lead to the situation
discussed in detail by Fabry and Kleitz [8], in which a reduction wave
with a sodium metal activity of 1 would propagate through the electro-
lyte until all transport gradients had been removed. The kinetic
hindrance of Eq. (32) can be inferred from a comparison of the chemical
coloration profiles of polycrystalline Na-β'' aluminas after 1 and
after 8 days of contact with molten sodium at 350°C, Fig. 3. These
profiles were determined by densitometry from micrographs of silver
stained cross sections of electrolytes contacted with Na. The method
is discussed in Ref. 11. The kinetic hindrance of the reaction

described by Eq. (32) thus produces a situation akin to that created by the immobile impurity whose presence was postulated in the determination of the chemical potential distribution. Equation (1) then describes a pseudo-equilibrium slowly evolving with time.

Also, the oxygen fugacity at the sulphur electrode/electrolyte interface, while not actually known, should be considerably higher than that of the sodium electrode, so that some transport number ratio gradient is expected to be maintained indefinitely. Thus, when the cells are being charged, processes could take place leading to internal Na deposition and associated microfracture as discussed in the previous section. The actual form of the gradient has not been determined but is probably more as assumed in Eq. (26) rather than in the discrete layer case. Eq. (31) for ΔV^{crit} could thus be considered at least as a qualitative if not a semi-quantitative guide for cell operation. The general trend of ΔV^{crit} in the discrete layer case is, however, of some use, since it appears to indicate that in the early stages of cell operation, when $\delta \ll \ell$, the Mode II degradation is unlikely.

While sensitive to the choice of p^x, Eq. (24) nevertheless can give some indication of what to expect for actual Na/S cells. For a typical Na/S battery, the charging current density is $0.1 A cm^{-2}$, $\sigma_i \cong 10^{-1} (\Omega cm)^{-1}$, and $\ell = 0.2$ cm so that $\Delta V \cong 0.2$ Volt. In the absence of polarization at the sulphur electrode/electrolyte interface, we would clearly have $\Delta V = 0.2$ volt $< \Delta V^{crit}$. In general, Mode II degradation could be avoided when

$$I\ell/\sigma_i \; < \; \Delta V^{crit} \tag{33}$$

where I is now the charging current density. One problem in the
application of Eq. (31) to the solid electrolyte in the Na/Na_2S_x
battery is that the electrochemical condition of the polysulphide/
electrolyte interface is usually not known. From the polarization
studies of Bones and Markin [15] and the work of Breiter and Dunn [16],
it would appear that the sulphur electrode/electrolyte polarization is
minimal for cells that are operating properly, i.e. no abnormal cell
resistances. However, improper cell operation or contamination
products might reduce $\Delta n_M^o/F$ significantly, so that ΔV^{crit}
would be lowered. Conditions at the sulfur electrode/electrolyte
interface thus can affect the degradation of the electrolyte. Eq. (33)
now permits us to indicate, at least qualitatively, which factors
contribute adversely to electrolyte degradation:

1. decrease in $\Delta n_M^o/F$, due to polarization at the sulfur
   electrode/electrolyte interface;

2. increased electrolyte resistance, due to contaminants or choice
   of electrolyte;

3. low local strength, due to improper fabrication processes;

4. increased current densities imposed during charging, due to
   improper cell management;

5. increased wall thicknesses, due to improper design.

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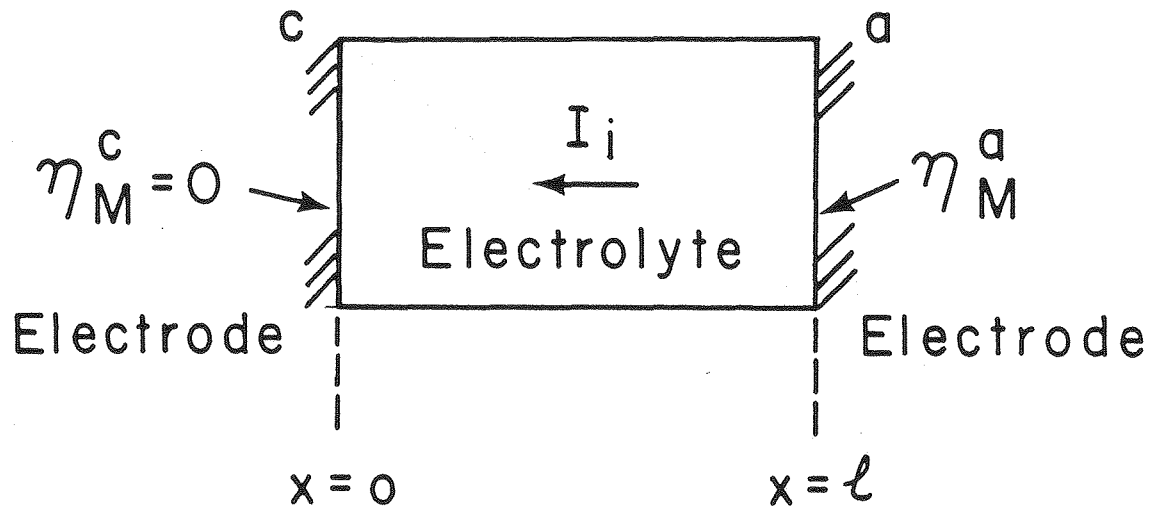14. M. S. Whittingham, J. Electrochem. Soc., $\underline{110}$, 1 (1976).

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SYMBOLS

e	electron
F	Faraday's constant
i	ions of M species, monovalent
I, I_i, I_e	total, ion, and electron currents
M	metal
ℓ	electrolyte thickness
p^x, p^c, p^a	ratio σ_i/σ_e at x, c, and a
r	ratio of I_i/I_e under steady state conditions
V_T	total applied voltage over electrolyte
V_T^{crit}	critical applied voltage over electrolyte
σ_i, σ_e	ionic and electronic conductivities
η_M, η_i, η_e	electrochemical potential of metal, ions and electrons
$\Delta\eta_M^0/F$	counter EMF over the electrolyte

FIGURE CAPTIONS
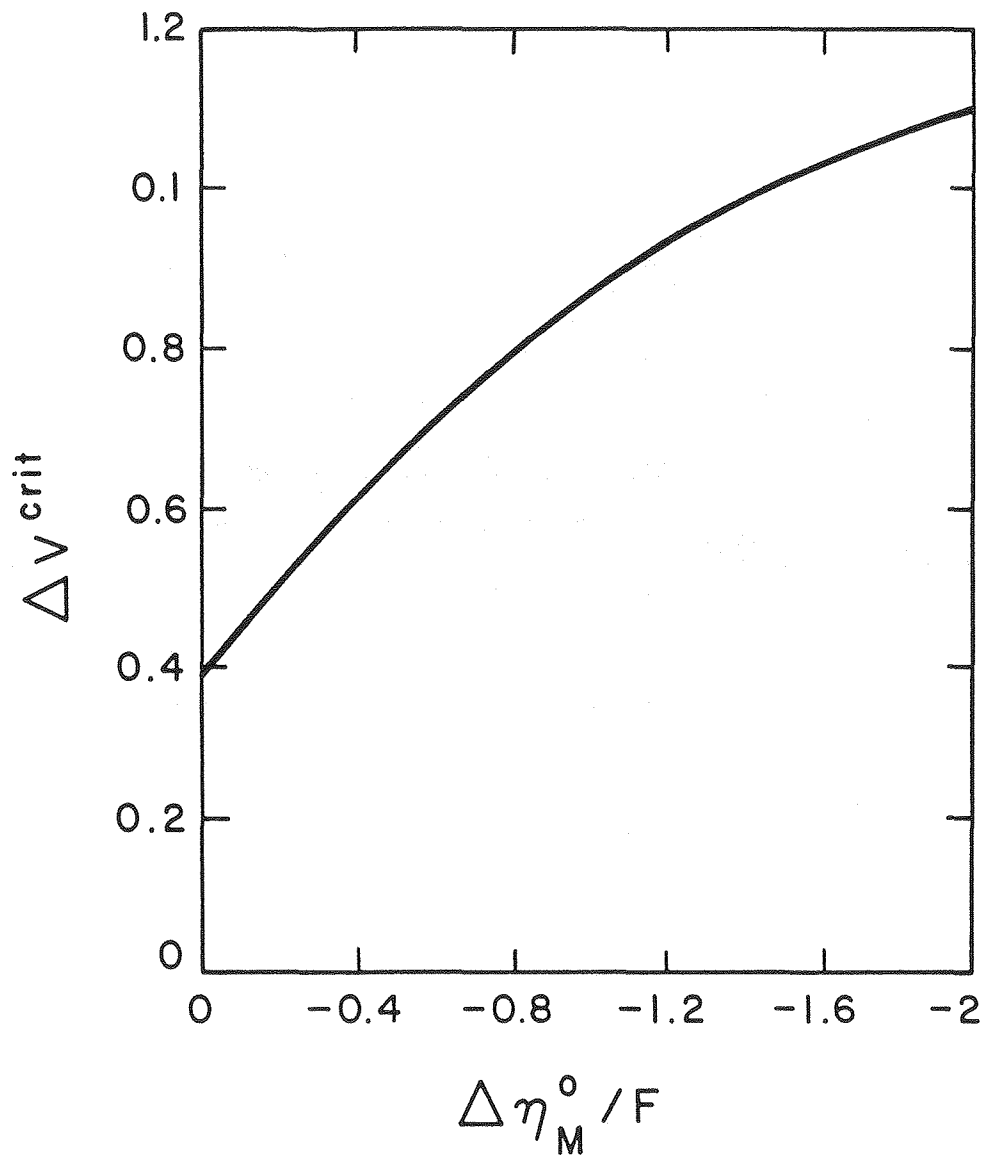
Figure 1. Electrolyte geometry.   XBL 812-159

Figure 2. Example of ΔV^{crit} versus $\Delta\eta_M^0/F$, for p^x as chosen in
Eq. (19).   XBL 814-757

Figure 3. Comparison of darkening profiles developed in sodium-β''
alumina polycrystalline electrolyte after 1 and 8 days of
contact with molten sodium at 350°C. The darkening was
enhanced by silver exchange. The profiles indicate a slow
surface reaction.   XBL 815-9530
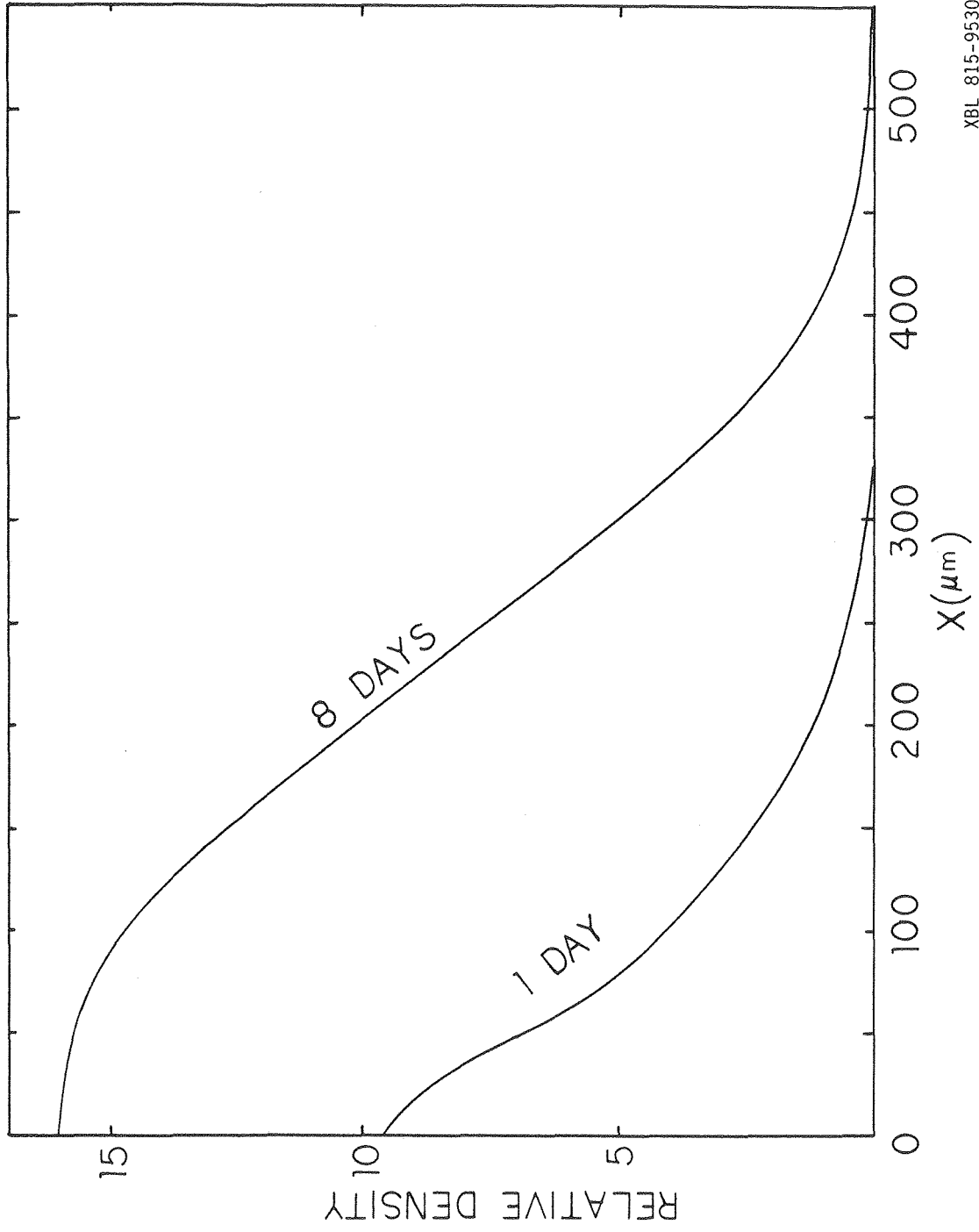
$$c \qquad \qquad a$$

$$\eta_M^c = 0 \rightarrow \qquad \overset{\displaystyle I_i}{\longleftarrow} \qquad \leftarrow \eta_M^a$$

Electrolyte

Electrode $\qquad$ Electrode

$$x = 0 \qquad \qquad x = \ell$$

XBL 812-159

Figure 1

The graph plots ΔV^{crit} on the vertical axis (ranging from 0 to 1.2, with tick labels 0, 0.2, 0.4, 0.6, 0.8, 0.1, 1.2) versus $\Delta \eta_M^0 / F$ on the horizontal axis (ranging from 0 to -2, with tick labels 0, -0.4, -0.8, -1.2, -1.6, -2).

XBL 814 - 757

Figure 2

Figure 3

XBL 815-9530