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IMPURITIES AND SOLID ELECTROLYTE FAILURE

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January 1982

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This work received support from the Assistant Secretary for Conservation and Renewables, Office of Advanced Conservation Technology, Electrochemical Systems Research Division, U. S. Department of Energy, under contract DE-AC03-76SF00098, and by the Electric Power Research Institute.

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Abstract

A thermodynamically based model is used to assess the effects of the formation of a layer of lowered ionic conductivity and increased electronic conductivity on the applied voltage at which solid electrolyte failure is to be expected. Such a layer can result from electrolyte contamination with electrode impurities. It is found that when a significant electrolyte resistivity increase is produced, electrolyte failure can be initiated by a mechanism that deposits sodium internally in the solid electrolyte. The results stress the necessity of operating solid electrolyte cells, such as Na/S, in a manner that minimizes electrode contamination.

I. Introduction

In a recent paper (1) the possible effects of current transport through a solid electrolyte containing a quasi-stationary gradient in ionic/electronic transport number gradient were discussed. Starting from the usual transport equations (2) it was shown that, under certain conditions, internal precipitation of metal could occur. This phenomenon could lead to a type of electrolyte failure called Mode II degradation (1,3,4). The recent treatment (1) considered a solid electrolyte, such as Na-β or β" alumina, in which the ionic conductivity*, σ_e^i, was uniform throughout and in which an increased electronic conductivity was present towards a negative metal electrode such as sodium. This model led to the identification of a critical threshold charging overvoltage, ΔV^{crit}, at which internal failure of the electrolyte could be expected. This threshold, when calculated for the case of Na-β" alumina solid electrolytes in a Na/S battery, was found to be well below the maximum voltage, or corresponding current density, that is expected in the charging cycle of a normally functioning Na/S cell. The presence of impurities do, however, appear to affect the critical voltage or current density thresholds unfavorably.

A particular problem occurring in solid electrolyte batteries operating at relatively high temperatures is that electrode

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

contamination products may partly penetrate the electrolyte. This can produce a layer in which the ionic conductivity may be significantly lowered. At the same time, the electronic conductivity in such a layer adjacent to the negative electrode could be expected to have increased, in the case of Na-β or β" aluminas, as a consequence of prolonged contact with the molten Na electrode (5). This case of contamination-reaction is examined here. An electrolyte is considered in which a quasi-stationary layer has formed of lowered ionic conductivity and increased electronic conductivity. As in the case of uniform ionic conductivity (1), the problem is again to calculate the distribution of the sodium chemical potential in the non-homogeneous electrolyte under conditions of current flow.

II. Chemical Potential Distribution

The electrolyte with its electrodes is shown in Figure 1. In the steady state the total ionic and electronic currents are constant so that:

$$I = I_i + I_e \tag{1}$$

Since I, I_i and I_e are constants everywhere in the electrolyte we also have

$$\frac{1}{x} \int_0^x (\sigma^i \nabla \eta_i / F) dx = \frac{1}{\ell} \int_0^\ell (\sigma^i \nabla \eta_i / F) dx \tag{2}$$

We need to find the chemical potential of the metal, M, at $x = \delta$, since, as follows from the layer case considered earlier (1), this chemical potential will reach its maximum at $x = \delta$. Thus, for the geometry shown in Figure 1:

$$\left(\frac{\ell}{\delta} - 1\right) \int_0^{\delta} (\sigma_1^i \nabla \eta_i / F) dx = \int_{\delta}^{\ell} (\sigma_2^i \nabla \eta_i / F) dx \tag{3}$$

For the assumed pseudo-equilibrium reaction $M \rightleftarrows i + e$, we have

$$\eta_i = \eta_M - \eta_e \tag{4}$$

so that from Eq. (3):

$$\left(\frac{\ell}{\delta} - 1\right) \sigma_2^i \int_0^{\delta} \nabla \eta_M dx - \sigma_2^i \int_0^{\ell} \nabla \eta_M dx =$$

$$\left(\frac{\ell}{\delta} - 1\right) \sigma_1^i \int_0^{\delta} \nabla \eta_e dx - \sigma_2^i \int_{\delta}^{\ell} \nabla \eta_e dx \tag{5}$$

Since:

$$\int_0^{\delta} \nabla \eta_M dx \equiv \Delta \eta_M^{\delta} \tag{6}$$

and

$$\int_{\delta}^{\ell} \nabla n_M dx \equiv \Delta n_M^0 - \Delta n_M^{\delta} \tag{7}$$

and

$$\int \nabla n_e dx = - I_e F \int \frac{1}{\sigma^e} dx \tag{8}$$

it follows that

$$\Delta n_M^{\delta} \left(1 + \frac{\sigma_2^i}{\sigma_1^i} \frac{\delta}{(\ell-\delta)}\right) = \frac{\sigma_2^i}{\sigma_1^i} \frac{\delta}{(\ell-\delta)} \Delta n_M^0 + \frac{\delta I_e F}{\sigma_i^e} \left[1 - \frac{\sigma_2^i}{\sigma_2^e}\right] \tag{9}$$

Also:

$$\int_0^x (\nabla n_e/F)\, dx \equiv -V_x = I_e \int_0^x \frac{1}{\sigma^e} dx \tag{10}$$

so that in the present geometry:

$$\int_0^{\ell} (\nabla n_e/F) dx \equiv -V_T = I_e \left(\frac{\delta}{\sigma_1^e} + \frac{(\ell-\delta)}{\sigma_2^e}\right) \tag{11}$$

or

$$V_T = -I_e \, \bar{\sigma}_e / \ell \tag{12}$$

where the average specific electronic conductivity, $\bar{\sigma}_e$, is defined by

$$\ell \bar{\sigma}_e^{-1} = \delta(\sigma_1^{\,e})^{-1} + (\ell-\delta)(\sigma_2^{\,e})^{-1} \tag{13}$$

From Eqs. 9-13 then follows that:

$$\Delta\eta_M^{\delta} = \left(1 + \frac{\sigma_2^{\,i}}{\sigma_1^{\,i}} \frac{\delta}{(\ell-\delta)}\right)^{-1} \left[\frac{\sigma_2^{\,i}}{\sigma_1^{\,i}} \frac{\delta}{(\ell-\delta)} \Delta\eta_M^{o} + \frac{\delta}{\ell} \frac{\sigma_2^{\,i}}{\sigma_1^{\,i}\sigma_2^{\,e}} \bar{\sigma}_e \, FV_T\right] \tag{14}$$

It has been assumed in Eq. (14) that $\sigma_2^{\,i} >> \sigma_2^{\,e}$. This assumption is quite valid for most solid electrolytes, such as sodium-beta aluminas, for which the properties have not been drastically modified.

Eq. (14) can also be written as

$$\frac{\Delta\eta_M^{\delta}}{F} = A\left[\frac{\Delta\eta_M^{o}}{F} + \frac{\ell-\delta}{\ell} \frac{\bar{\sigma}_e}{\sigma_2^{\,e}} V_T\right] \Big/ (1+A) \tag{15}$$

where

$$A = \frac{\sigma_2^{\,i}}{\sigma_1^{\,i}} \frac{\delta}{(\ell-\delta)} \tag{16}$$

and $\Delta\eta_M^\delta/F$ has the dimension of volts.

If we assume further that $\sigma_1^e >> \sigma_2^e$ then we have

$$\bar{\sigma}_e = \sigma_2^e \, \ell/(\ell-\delta) \tag{17}$$

This is an assumption similar to the one made previously (1). For the case of beta alumina, this condition would be satisfied if $\sigma_1^e \geq 10\sigma_2^e$. This is not difficult to envisage, since at 300°C σ_2^e is in the neighborhood of 10^{-13} to 10^{-15} $(\Omega cm)^{-1}$ (6,7). Eq. (15) can then finally be written simply as:

$$\frac{\Delta\eta_M^\delta}{F} \cong \frac{A}{(1+A)} \left(\frac{\Delta\eta_M^o}{F} + V_T \right) \tag{18}$$

III. Discussion

Eq. (18) shows that internal sodium formation in the solid electrolyte can occur if V_T and A are sufficiently large so that $\Delta\eta_M^\delta/F \geq 0$. The metallic sodium, which presumably could start forming at internal flaws such as pores, will eventually reach a pressure $P \simeq \Delta\eta_M^\delta/V_M$. At that point further internal deposition has been stopped since by then the mechanical counter potential balances the electrical driving force. In the expression for P, the precipitating metal has been assumed to be incompressible; this is a reasonable approximation for metals. Local failure would occur if P is sufficiently high so that stresses at the internally pressurized flaws exceed the critical stress intensity factor (8). Since flaw geometries can vary widely,

the critical pressure cannot be given accurately; it will depend significantly on the electrolyte preparation method and microstructure, and will be statistically distributed. One might expect the critical value of P to be proportional to the mechanical strength of the electrolyte. When $\Delta\eta_M^{\sigma}/F = 0.1$ V, e.g., then P would reach about $4 \times 10^8 N/M^2$ (~ 57,000 psi). It is assumed here that this would be an average critical value for a carefully prepared electrolyte in which residual internal stresses have been reduced by some annealing process. At this point the applied voltage, V_T, will have reached a positive value of V_T^{crit} opposing the negative counter EMF of the cell, $\Delta\eta_M^{o}/F$. One may then define a critical charging overvoltage $\Delta V_T^{crit} = \Delta\eta_F^{o}/F + V_T^{crit}$. Figure 2 shows the dependence of ΔV_T^{crit} on the parameter A, assuming that the critical internal pressure P was reached when $\Delta\eta_M^{\delta}/F = 0.1$ V. Since, in the Na/S battery, the resistance overvoltages during changing are usually on the order of a few tenths of a volt, a maximum permissible charging overvoltage $\Delta V_T^{max} = 0.5$ V has been chosen. This would be associated with electrolyte failure initiation by internal Na deposition at a value of $A \simeq 0.2 - 0.3$. If we assume, for the sake of illustration that A could reach this value for $\delta << \ell$, then for $\ell = 2$ mm and $\delta = 10\mu m$, A would be equal to 2.5 with $\sigma_2{}^i/\sigma_1{}^i = 50$. For Na-β or β" aluminas impurities are known that substantially decrease the ionic conductivity; calcium is one such impurity (9-12) that could produce high values of $\sigma_2{}^i/\sigma_1{}^i$.

If the critical condition is written as a maximum permissible electrolyte overall resistance increase then a very simple relationship

results for the case considered here. The overall ionic resistance may be written as:

$$R_i = \delta/\sigma_1{}^i + (\ell-\delta)/\sigma_2{}^i \tag{19}$$

so that from Eq. (16), with $\delta \ll \ell$ and $A = 0.25$ at $\Delta V_T^{crit} = 0.5$ V we find

$$R_i^{crit} \cong 5\ R_i^o \tag{20}$$

where R_i^o is the initial, uniform ionic resistivity of the pure solid electrolyte. Eq. (20) thus indicates that if a substantial electrolyte resistance develops in a cell, as a consequence of the contamination process described here, electrolyte failure is to be expected. Since the failure mechanism does not strongly depend on δ/ℓ in the case where $\sigma_2{}^i/\sigma_1{}^i \gg 1$, one might suspect that the rise in R_i would be controlled by the contamination rate of the Na electrode in Na/S cells, and thus by the corrosion rate of the container or current collector. Possibly, impurities such as calcium, contained in second phases in the electrolyte and redistributed during the cell operation could have the same effect. Resistance rises due to Ca contamination have been recently reported by Bugden et al. (10). It is commonly observed that resistance rises precede cell failure. A possible sequence of events leading to failure thus might be: near surface electrolyte reduction by Na, introducing an increased electronic conductivity layer;

contamination increasing the ionic resistivity of surface layer; initiation of a subsurface crack by internal Na deposition; extension of this crack to the Na electrode; rapid crack growth by a Mode I (3) mechanism.

The model presented here, when applied to Na/S cells with Na-β or β" alumina electrolytes thus suggest that continued development should be directed towards improvement of electrochemical corrosion resistances of the cell materials and to the lowering of initial impurity levels in the electrode as well as the electrolyte.

Acknowledgments

This work received support from the Assistant Secretary for Conservation and Renewables, Office of Advanced Conservation Technology, Electrochemical Systems Research Division, U. S. Department of Energy, under contract DE-AC03-76SF00098, and by the Electric Power Research Institute.

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
R_i	total ionic resistivity of electrolyte
R_i^o	ionic resistivity of pure electrolyte
R_i^{crit}	total ionic resistivity at $V_T = V_T^{crit}$
V_T	total applied voltage over electrolyte
V_T^{crit}	critical applied voltage at failure initiation
ΔV_T^{crit}	critical applied electrolyte resistance overvoltage
ΔV_T^{max}	maximum permissible charging overvoltage
σ^i, σ_i^e, $\bar{\sigma}_e$	ionic, electronic, average electronic specific conductivities
η_M, η_i, η_e	electrochemical potential of metal, ions, and electrons
$\Delta\eta_M^\delta$	chemical potential of M at $x = \delta$
$\Delta\eta_M^o/F$	counter EMF over the cell

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Figure Captions

Figure 1. Electrolyte geometry. The cathode has a metal activity of 1 so that $\eta_M^c = 0$. The electrolyte is shown for a charging condition. In each segment of the electrolyte the indicated conductivities are assumed constant.

Figure 2. Plot of the parameter A versus the critical applied charging overvoltage ΔV_T^{crit}. The curve divides the field in two domains where failure is or is not expected. The maximum permissible charging overvoltage, ΔV_T^{max}, is determined by the electrolyte resistivity and by the charging current density.

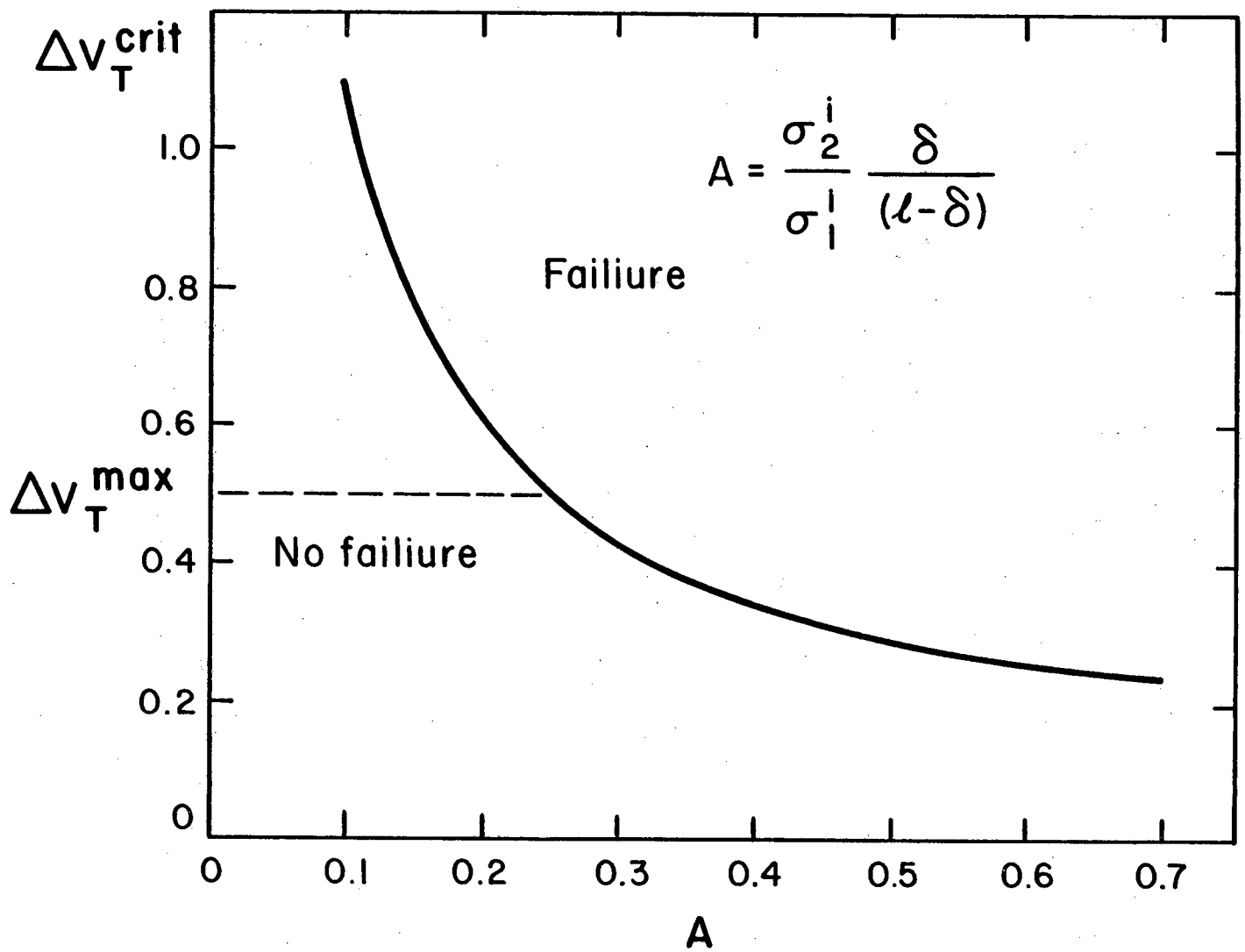

Figure 1

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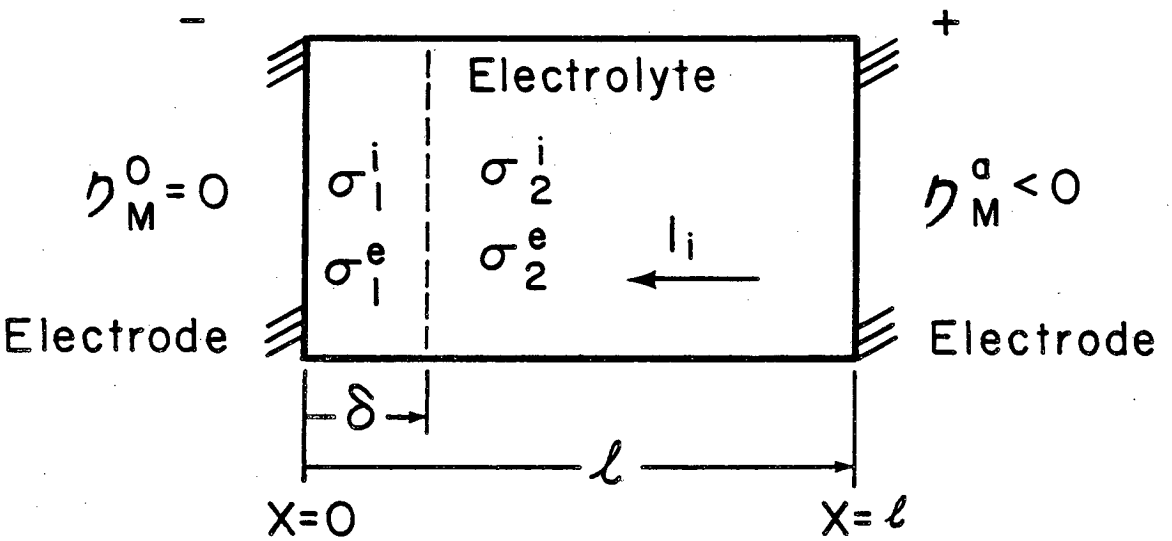

Figure 2

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