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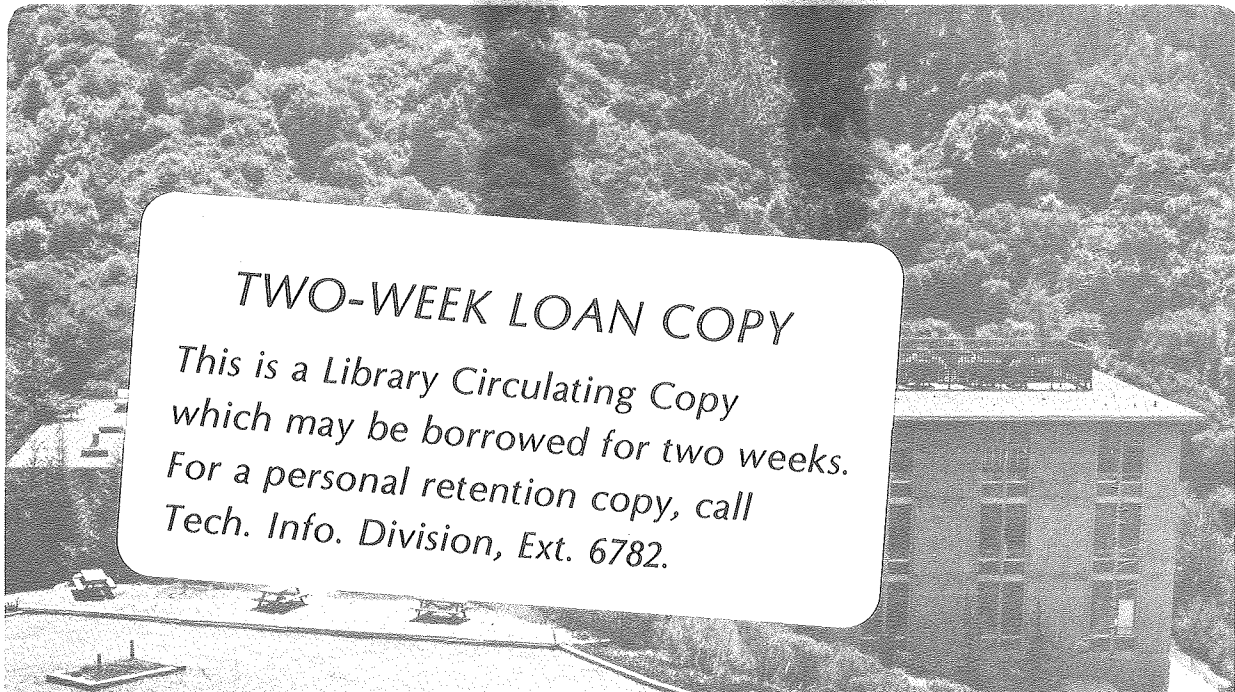
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Abstract

Ion conduction is considered through electrolytes containing an immobile gradient in the electronic/ionic transport number ratio. It is shown that internal deposition at 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 sodium-beta alumina electrolytes leads to identification of factors that could contribute to electrolyte degradation.

TRANSPORT NUMBER GRADIENTS AND SOLID ELECTROLYTE DEGRADATION

Lutgard C. DeJonghe

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 (Mode I) or to internal sodium formation (Mode II) [2]. In other materials the electric current may only produce donor ionization or electron-acceptor recombination [3]. 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 is a wide band gap semiconductor in which an immobile gradient in electronic conductivity has been produced by a shallow donor, e.g. by chemical diffusion at high temperature, and if the permissible deviation from stoichiometry for the highly mobile ions carrying the current is negligibly small. We consider this here, following an analysis of Choudhury and Patterson [4], and show that at low applied voltages or low current densities, internal electrolysis with formation of the reduced metal phase may be possible.

II. Chemical Potential Distribution

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



Transport in such a solid can be described by

$$I_i = -\sigma_i \nabla \eta_i / F \quad (2)$$

and

$$I_e = \sigma_e \nabla \eta_e / F \quad (3)$$

provided it is assumed that one particle current is independent of the other's gradient in chemical potential. Under these conditions the partial conductivities σ_i and σ_e are constants that are determined 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 currents 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 [5], but it will not be considered here.

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

Following Choudhury and Patterson we can define

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

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

$$I = \frac{\sigma_i (1+r)}{F r} (\nabla \eta_M - \nabla \eta_e) \quad (5)$$

r is the parameter that characterizes the steady state. In Eq. (5) we used the relationship $\eta_M = \eta_i + \eta_e$ that follows from Eq. (1) in local equilibrium.

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

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

so that from (5) and (6)

$$\nabla \eta_e = - \frac{\sigma_i}{(r\sigma_e - \sigma_i)} \nabla \eta_M \quad (7)$$

The value of r follows from integrating both sides of Eq. (7) over the length of the sample from $x = 0$ at c to $x = \ell$ at a (Fig. 1). If we put the negative electrode, c , in the standard state for the metal M , then $\eta_M^c = 0$. For a total applied voltage, V_T , with $\Delta \eta_M^0 =$ chemical potential difference over the electrolyte and with $p^x = \sigma_i / \sigma_e$ and $p^x = p^c + bx$, where $b = (p^a - p^c) / \ell$, one obtains

$$r = p^a \left(1 - \frac{\nabla n_M^0}{V_T F} \right) \quad (8)$$

The conservation of ions anywhere in the sample can be expressed as:

$$I_i = \frac{\sigma_i}{x} \int_0^x \left(\frac{\nabla n_M}{F} + \frac{\nabla n_e}{F} \right) dx \quad (9)$$

where σ_i is taken to be constant. Since I_i is constant one also gets

$$I_i = -\frac{\sigma_i}{\ell} \int_0^\ell \left(\frac{\nabla n_M}{F} + \frac{\nabla n_e}{F} \right) dx \quad (10)$$

Eqs. (9) and (10) then follows that

$$n_M(x) = \frac{x}{\ell} \nabla n_M^0 - \frac{x}{\ell} V_T F + V_x F \quad (11)$$

V_x can be found from Eq. (7):

$$V_x = \frac{I}{(1+r)} \int_0^x \frac{1}{\sigma_e} dx \quad (12)$$

from which:

$$V_x = V_T \left[\int_0^\ell \frac{1}{\sigma_e} dx \right]^{-1} \int_0^x \frac{1}{\sigma_e} dx \quad (13)$$

Evaluation of V_x follows straightforwardly with the simple assumed dependence of σ_e and σ_i ; as before:

$$\frac{\sigma_i}{\sigma_e} = p^c - \frac{(p_i - p_a)}{\ell} x \quad (14)$$

Eq. (11) then yields with Eq. (13):

$$\eta_M(x) = \frac{x}{\ell} \eta_M^0 - FV_T \frac{x}{\ell} \frac{p^a - p^x}{p^a + p^c} \quad (15)$$

It is thus seen that the local value of η_M is simply what it would have been under open circuit conditions modified by a term that depends on the transport number gradient and the applied voltage. If V_T is opposed to $\Delta\eta_M^0$, i.e. a charging condition, then, for $p^x < p^a$, we get $\eta_M(x) > \frac{x}{\ell} \Delta\eta_M^0$. $\eta_M(x)$ can in principle reach a positive value, so that M could be formed inside the electrolyte, under pressure. If M is considered to be incompressible a pressure $P(x)$ would be generated equal to $P(x) = -\eta_M(x)/v_M$, where v_M is the molar volume of M. For $\eta_M/F = 1$ volt a corresponding pressure is 4×10^9 N/M² (~570,000 psi). This exceeds the fracture strength of any solid electrolyte by about an order of magnitude.

Since $\eta_M(x)$ depends on x , we have to find its maximum value, η_M^{\max} . η_M^{\max} follows readily from putting $\partial\eta_M(x)/\partial x = 0$. An additional simplification follows from the plausible assumption that $p^a \gg p^c$ when p^a is near the intrinsic value of the wide band gap electronic insulator under consideration. Then one finds

$$\eta_M(x) \approx \frac{x}{\ell} (\Delta\eta_M^0 - FV_T) + FV_T \frac{x^2}{\ell^2} \quad (16)$$

and

$$\eta_M^{\max} = (FV_T - \Delta\eta_M^0)^2 / 4FV_T \quad (17)$$

at

$$\frac{x}{l} = (FV_T - \Delta\eta_M^0) / 2FV_T \quad (18)$$

If we use as a criterion, somewhat arbitrarily, that internal fracture due to electrolysis generated pressure of M would occur at $\eta_M^{\max} = 0.05\Delta\eta_M^0$, then one would obtain a critical charging voltage V_T^{crit} from Eq. (17):

$$V_T^{\text{crit}} \approx 1.5\Delta\eta_M^0 / F \quad (19)$$

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

Recently De Jonghe et al. [2] reported a slow degradation of sodium-beta alumina solid electrolytes that appeared to take the form of an internal sodium deposition inside the electrolyte with associated microcracking. It is thought that the above analysis may apply to this type of degradation (Mode II).

When sodium-beta aluminas are in contact with molten sodium they are partly reduced. The process was found to involve oxygen removal from the electrolyte, leaving oxygen vacancies compensated by electrons [6]. This process of reduction is quite slow, and propagates through the electrolyte at a rate determined by the oxygen vacancy mobility and the applied field. 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 [7], 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 equilibration described in Eq. (1) is strongly rate limited, so that a pseudo-equilibrium, slowly evolving with time, could be considered to be established. It should be noted that the process of electrolyte reduction by the sodium electrode proceeds slowly through the electrolytes. Even after a substantial amount of charge transfer the chemical coloration associated with increased electronic conductivity has not

yet fully propagated through the entire wall thickness of the electrolytes. This clearly indicates that the reaction described by Eq. (1) is a very slow one, so that the highly mobile sodium ion can be considered to establish a pseudo-equilibrium permitting an electronic transport number gradient to exist for a considerable time. If the reaction (1) would be fully equilibrated, then a situation would arise as discussed in detail by Fabry and Kleitz [3] in which a reduction wave with sodium metal activity of 1, would propagate through the electrolyte until all transport number gradients had been removed. The situation for sodium-beta alumina solid electrolytes used in sodium/sodium polysulphide batteries is thought to be in between the two extremes mentioned here. Equation (19) is therefore a lower bound to the critical voltage at which the Mode II degradation could be initiated by current passage through the electrolyte containing an electronic transport number gradient.

One problem in the application of Eq. (19) to the solid electrolyte Na/Na₂S_x battery is that the electrochemical condition of the polysulphide/electrolyte interface is usually not known. From the polarization studies of Bones and Markin [8] and the work of Breiter and Dunn [9], it would appear that the sulphur electrode/electrolyte polarization is minimal for cells that are operating properly, i.e. no abnormal cell resistance increases. For an electrolyte with a specific resistivity of 5 Ω cm, and a wall thickness of 0.2 cm, the actual charging overvoltage over the electrolyte itself, ΔV, would be about 0.1 volt at 0.1 A/cm². We could rewrite Eq. (19) as:

$$\Delta V^{\text{crit}} = V_T^{\text{crit}} - \Delta \eta_M^0 \quad (18)$$

where now ΔV^{crit} is the critical electrolyte resistance overvoltage needed to drive the charging current through the electrolyte. With $\Delta \eta_M^0 \approx 2$ volts for Na/Na₂S_x, this would make $\Delta V^{\text{crit}} \approx 1$ volt.

It is thus seen that under normal operating conditions with $V_T < 2.5$ volt, Mode II degradation would probably not lead to internal microfracturing of the electrolyte. If, however, interface polarization occurred due to, e.g. impurity deposition, then Model II could be activated. From the considerations given above, we could give a qualitative indication of the factors which must be expected to adversely affect the electrolyte degradation by a Mode II mechanism when the cell is operated at a constant current density:

1. High charging current densities leading to an increased ΔV over the electrolyte.
2. Increased electrolyte thickness.
3. Increased electrolyte resistance.
4. Polarization phenomena at the sulphur/electrolyte interface, leading to a lowered $\Delta \eta_M^0$.

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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 length
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	applied voltage over electrolyte
V_T^{crit}	critical applied voltage over electrolyte
σ_i, σ_e	ion and electron conductivities under Ohmic conditions.
η_M, η_i, η_e	electrochemical potential of metal, ions and electrons
$\Delta\eta_M^0$	counter EMF over the electrolyte

FIGURE CAPTIONS

Figure 1. Electrolyte geometry.

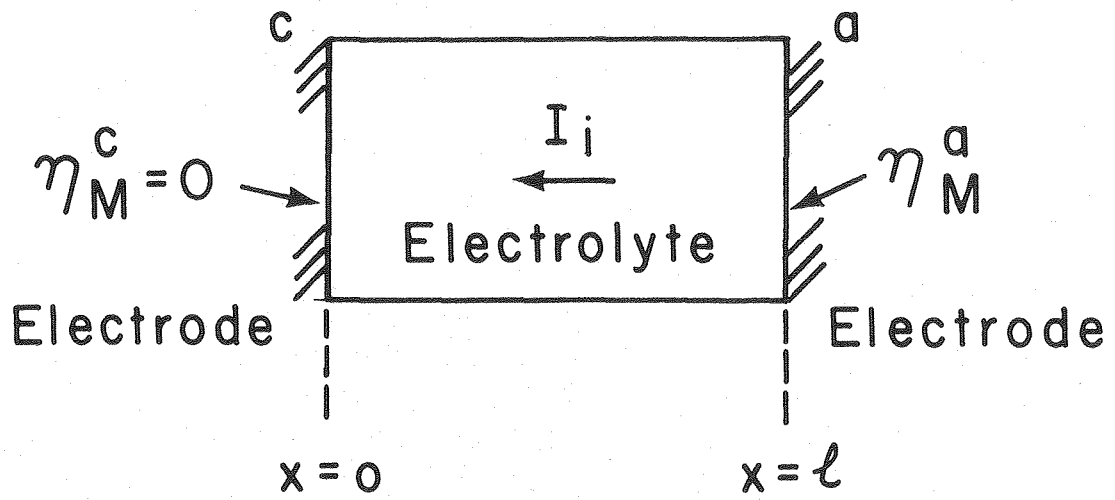


Figure 1

XBL 812-159

