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OXYGEN DEPLETION AND SLOW CRACK GROWTH IN
SODIUM BETA"-ALUMINA SOLID ELECTROLYTES

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ABSTRACT

Slow crack growth in sodium-beta"alumina solid electrolytes is considered resulting from oxygen depletion at the tip of a sodium-filled crack during sodium electrolysis. Extreme depletion of oxygen may lead to a destructive reduction of the electrolyte at the crack tip, thus producing slow crack propagation. The time dependent and steady state oxygen concentration profiles in the sodium electrode are calculated and related to a flaw size for slow crack propagation.

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INTRODUCTION

When a sodium ion current through sodium beta"-alumina solid electrolyte exceeds some critical value, cracking may result. This degradation has been attributed to propagation of pre-existing surface cracks, driven by the Poiseuille pressure that is generated when sodium metal, formed electrolytically inside the crack, flows out to the sodium electrode.(1) The rate of flow of sodium is proportional to the current density, so above some current density, when the stress intensity at the crack tip exceeds what the electrolyte can support mechanically, the pre-existing surface flaws should propagate (2, 3, 4). Molten sodium was at first not thought to attack beta"-alumina chemically, but more recently, changes in the surface appearance of the electrolyte after exposure to molten sodium have been reported. After sessile drop experiments, the Na beta"-alumina under the sodium drop was smoother than the surrounding electrolyte (5). Also, electrolyte was pitted after cycling in sodium/sulfur cells for 200 Ah/cm² (6). In addition, weight loss after immersion in molten sodium could indicate that beta"-alumina has a small solubility in sodium (7).

Acoustic emission monitoring of electrolytes carrying ionic currents indicated that the critical current density at which cracks begin to propagate depended on the time for which cells had been cycled and on the rate at which current densities were increased (8). These findings indicated that some type of slow degradation can contribute to the propagation of cracks.

A degradation model based on stress corrosion was proposed by Richman and Tennenhouse (RT) (9), who assumed that the electrolyte was soluble to a slight degree in the sodium and that sodium, as it flowed out of the crack, would carry away dissolved electrolyte from the crack tip. In the RT model the total flux of dissolved electrolyte depended on three terms: first, the removal of electrolyte by sodium flowing out of the crack; second, the chemical potential of the electrolyte which would be raised due to Poiseuille pressure generated by the flowing sodium, thus increasing the dissolution rate of the electrolyte at the tip; finally, the chemical potential of the electrolyte which would be lowered at the crack tip due to the small radius of curvature, causing a redeposition of solute which opposes the other fluxes. At low current density, the electrolyte deposition rate at the crack tip would exceed the fluxes out of the crack, and no crack growth or crack blunting would be expected, but at high current density the stress and the flow terms would be larger and the crack would grow. However, around 300 C, beta"-alumina apparently does not exhibit a detectable slow crack growth when statically immersed and mechanically stressed in sodium (10), indicating that the effect of mechanical stress only on the crack tip velocity is not strong. Thus, the RT model, while predicting a current density threshold for crack growth, is in its present formulation, unlikely to describe the critical current densities at which catastrophic failures were observed.

Oxygen Depletion

A possible corrosion mechanism that can contribute to slow crack growth is destructive chemical reduction of the electrolyte. Normally, the sodium used in testing electrolyte is nearly saturated with oxygen, setting the oxygen fugacity at about 10^{-62} atmospheres at 300°C . Beta"-alumina is reduced to some degree even by static immersion in sodium saturated with oxygen, (11) and the degree of reduction should depend on the oxygen fugacity.

At the exit electrolyte/sodium interface of a Na/S cell new sodium, which does not contain oxygen, is formed electrochemically during the charging cycle. The existing dissolved oxygen is swept away at a velocity equal to the rate of formation of sodium,

$$v = j V_m / F \quad \text{Eqn. (1)}$$

where j is the current density, V_m is the molar volume of sodium, and F is Faraday's constant. Then, the existing dissolved oxygen diffuses back into the solute-free sodium, so the oxygen concentration follows the equation of convection and diffusion which, in one dimension, is

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \quad \text{Eqn. (2)}$$

where D is the chemical diffusion coefficient of oxygen in molten sodium, v the velocity from equation Eqn. 1, x is the distance from the electrode/electrolyte interface, t is the time for which the current

has been passed, and c is the concentration of dissolved oxygen. The solute cannot pass through the electrolyte or the container, so the initial condition is $c = c_0$ for all x , and the boundary conditions are

$$D \frac{\partial c}{\partial x} = vc \quad \text{at } x = 0$$

and

$$c = c_0 \quad \text{for } x \rightarrow \infty$$

Eqn. (3)

The problem is identical to the settling of particles in a suspension under the influence of gravity and Brownian motion, for which solutions are available. Mason and Weaver (12) give the solution as:

$$\begin{aligned} c/c_0 = & \frac{-v\sqrt{t}}{\sqrt{D\pi}} \exp -[(vt - x)^2/4Dt] + \frac{1}{2} \left[1 - \operatorname{erf} \left(\frac{vt - x}{\sqrt{4Dt}} \right) \right] \\ & + \frac{1}{2} \exp \left(\frac{vx}{D} \right) \left[1 + \frac{v}{D} (vt + x) \right] \left[1 - \operatorname{erf} \left(\frac{vt + x}{\sqrt{4Dt}} \right) \right] \end{aligned} \quad \text{Eqn. (4)}$$

For $D = 5 \times 10^{-9} \text{ m}^2/\text{sec}$ and $j = 10^3 \text{ A/m}^2$, the concentration profiles at various times are shown in Figure 1. After 24 hours, the concentration of solute at the surface is 0.35 of the initial concentration. The important factor for the degradation process by reduction is the oxygen concentration at the electrolyte/sodium interface, and this is shown for a variety of current densities and times in Figure 2. It is clear that high current densities would be needed to depress rapidly the oxygen fugacity at the planar interface. High sodium flow velocities can, however, occur in cracks at ordinary current densities.

Feldman and De Jonghe (3), showed that inside a surface flaw or crack, the sodium flow velocity is increased by a factor ℓ/r compared to the velocity at the electrolyte surface shown by Eqn. 1, where ℓ is the crack length and r is half the crack opening displacement, so that inside the crack,

$$v = (j V_m / F) (\ell / r) \quad \text{Eqn. (5)}$$

and

$$1/r = \frac{1 E' F}{5.44 j V_m \eta} \quad \text{Eqn. (6)}$$

where E' is Young's modulus of beta-alumina (200 GPa) and η is the viscosity of sodium (3.4×10^{-4} kg/m sec at 300°C)

For $\ell = 100$ micrometers and $j = 10^3$ A/m², and with $V_m = 2.37 \times 10^{-15}$ m³/mol, ℓ/r is 1.2×10^4 . In this case, the boundary conditions are changed: the velocity at the crack exit would be given by Eqn. 1, so the solute concentration will not change very rapidly there. For the crack geometry shown in Figure 3, the boundary conditions would be:

$$\begin{aligned} D \frac{\partial c}{\partial x} &= v c, & x &= 0 \\ c &= c_0, & x &= \ell \end{aligned} \quad \text{Eqn. (7)}$$

and the equation will be much more difficult to solve because the second boundary condition is not homogeneous. As an approximation, it is possible to use another solution from Mason and Weaver (12) for the

settling of particles in a suspension of finite depth ℓ' , with the boundary conditions

$$D \frac{\partial C}{\partial x} = vC \quad , \quad x = 0 \quad , \quad \ell' \quad \text{Eqn. (8)}$$

and to use a depth ℓ' longer than the crack length such that the concentration at the crack opening, where $x = \ell$, remains approximately constant. Then the solution is:

$$\begin{aligned} c/c_o = & \frac{v\ell' \exp \frac{vx}{D}}{D \left[\exp \left(\frac{v\ell'}{D} \right) - 1 \right]} + 16D^2 v \pi \ell'^3 \exp \left(\frac{vx}{2D} \right) \sum_{n=1}^{\infty} \\ & \frac{\exp \left[\frac{(4D^2 n^2 \pi^2 + v^2 \ell'^2) t}{4 D \ell'^2} \right] n \left[1 - (-1)^n \exp \left(\frac{-v\ell'}{2D} \right) \right] \left[v \sin \frac{n\pi x}{\ell'} + \frac{2n\pi D}{\ell'} \cos \frac{n\pi x}{\ell'} \right]}{[4D^2 n^2 \pi^2 + v^2 \ell'^2]^2} \end{aligned} \quad \text{Eqn. (9)}$$

For $j = 10^3 \text{ A/m}^2$, $\ell = 100 \text{ micrometers}$, and $\ell/r = 1.2 \times 10^4$, ℓ' is about 108 micrometers, and after 2 seconds the concentration of solute is 0.02 of its initial value; after one minute it reaches a steady state of 10^{-20} of the initial value. Because the steady state concentration is reached so rapidly relative to the duration of a normal charging cycle, the time dependent term of Eqn. 9 can be ignored and only the first term, giving the steady state concentration, need be used. The steady state concentration at the crack tip, C_i , for low values of the dimensionless parameter $v\ell'/D$ is shown in Figure 4. For a practical current density, e.g. 10^3 A/m^2 , C_i/C_o would rapidly reach 10^{-240} , sufficient to reduce even alpha-alumina at 300°C .

Because the concentration at the crack opening varies slowly with time according to Eqn. 4, C_0 in Eqn. 9 could be replaced by the concentration at the interface, obtained from Eqn. 4, lowering further the oxygen concentration. Thus, the oxygen concentration in a crack can be substantially diminished by the flow of sodium out of the crack, and some effect on the degradation process might be expected. The above estimate has ignored the possible oxygen source provided by the electrolyte. This would tend to raise the oxygen fugacity.

The steady state oxygen fugacity estimates would indicate that the potential for destructive reduction and thus slow crack growth, is always present at practical charging current densities, except for surface flaws for which $v\ell'/r$ is substantially lower than, say, 200. However, it has been observed that electrolytes can be used for very extended periods, without formation of any form of degradation developing at the sodium side. An example of such an electrolyte has been shown in Figure 5. This electrolyte was tested by the Ford Aeronutronics group for over one year, for a total of 592 Ahr/cm^2 of charging, at about 10^3 A/cm^2 . The absence of any form of degradation indicates, in the context of the present analysis, that an oxygen fugacity threshold should exist above which destructive reduction does not occur. Such a threshold, of course, exists for any oxide. A stability study of beta-aluminas in oxygen potential gradients has been done by Jacob, (14) indicating that at some oxygen potential the electrolytes can decompose. Unfortunately, the stability domain of beta-aluminas versus oxygen, in contact with molten sodium is not

known. It is estimated that the sodium beta-aluminas would be less stable than alpha alumina, but more stable than titania. This would put the threshold fugacity for destructive reduction, corresponding to C_{cr} , about a factor 10^{-20} lower than that of the sodium/sodium oxide equilibrium.

The calculations by Feldman and De Jonghe (3) have shown that ℓ/r is not very sensitive to crack length and is about equal to 10^4 . The dimensionless group $v\ell'/r$ will thus depend mainly on the value of ℓ' . If it is assumed that ℓ' is about equal to the crack length, ℓ , then, using Eqn. 9, an approximate relationship for the steady state interface oxygen fugacity may be written as:

$$\ln (C_i/C_o) \approx \ln (v\ell/D) - v\ell/D + 1 \quad \text{Eqn. 10}$$

where, using the appropriate values (in MKS units) in Eqn. 6:

$$v\ell/D \approx 500 j\ell \quad \text{Eqn. 11}$$

An estimate might now be made of the critical flaw size for onset of slow degradation, at some current density, j . If it is then estimated, as suggested above, that the destructive reduction threshold is on the order of $C_{cr}/C_o = 10^{-20}$, then Eqn. 10 permits an estimate of the critical flaw length. The estimated values are shown in Table I. The critical flaw size at a charging current density of 1000 A/m^2 would be between 50 and 100 micrometers. It is interesting to note that this is near the size of the largest grains that can develop in the usual electrolytes during fabrication, as a result of abnormal grain growth.

Large grains have been shown to be failure initiation sites (11,13), since surface flaws are commonly on the order of the grain size.

The analysis presented here thus indicates the possibility of slow crack growth associated with oxygen depletion in cracks above some critical size. It also underscores the necessity of careful microstructural control during the processing of the ceramic electrolyte, so that grains and other flaws with a size exceeding about 50 micrometers are absent in the electrolyte surface exposed to the sodium electrode.

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Figure Captions

1. Concentration profile of dissolved oxygen near the Na/electrolyte interface vs. time for various current densities.
2. Dissolved oxygen concentration at the Na/electrolyte interface vs. time for various current densities.
3. Geometry of the sodium filled flaw.
4. Steady state oxygen concentration at the crack tip vs. vl'/D .
5. Cross section of sodium beta"-alumina electrolyte tested in a Na/S cell for a total of 5.92×10^4 Ahr/m² of charging cycles at about 10^3 A/m². This electrolyte, tested by Ford Aeronutronics, is free of any form of degradation.

TABLE I

j A/m ²	ℓ (micrometer)				
	10	20	50	100	200
500	-0.3	-1	-4	-9	-20
1000	-1	-3	-9	-20	-41
2500	-4	-9	-25	-52	-106
5000	-9	-20	-52	-106	-215

Relative oxygen activity at the crack tip, $\log_{10}(C_i/C_o)$, as a function of current density, j , and crack length, ℓ .

Figure 1

XBL 853-10137

XBL 853-10135

Figure 2

XBL 853-10136

Figure 3

XBL 853-10133

Figure 4

Figure 5

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