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On some aspects of breakdown of β''-alumina solid electrolyte

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A theoretical expression is derived for the pressure generated in the sodium-filled cracks of β''-alumina under electrolytic conditions by treating the flux of sodium ions to the cracks in terms of the Laplace equation for the appropriate boundary conditions. It is demonstrated that the pressure generated decreases with increasing crack length for a given current density in contrast to the predictions of some investigators. It is suggested that some other factors must be considered if the microfracture model via Poiseuille pressure is to be a viable mechanism for electrolyte degradation.

1. Introduction

It has been known for some time that the premature failure of sodium–sulfur cells can often be traced to the failure of the solid electrolyte membrane. Several models which attempt to describe the failure of the electrolyte have been proposed to date [1–4]. Common to them all is the concept of ion focussing and the resultant development of Poiseuille pressure which presumably helps the crack grow. There are also some very fundamental differences in the proposed mechanisms of degradation. Richman and Tennenhouse [2] proposed that crack propagation occurs by preferential dissolution of β-alumina at the crack tips. Richman and Tennenhouse [2] were able to demonstrate that extremely small solubilities can lead to significantly large crack propagation rates. Others [3, 4] have argued in favour of a pressure driven crack model. In view of the limited data available at the present time, coupled with several uncertainties associated with causes of actual cell failures, convincing arguments can be made in favour of either type of model: stress-assisted corrosion or a pressure driven crack. All of these authors have assumed in their modelling that the crack is tip fed with sodium ions. This assumption has been met with some (rightful) criticism [5]. One of the objectives of the present paper is to relax this restriction and determine the flux of sodium ions to the sodium filled crack by solving the Laplace equation for appropriate boundary conditions. Recently, Brennan [6] examined the problem of the crack being fed from the sides. His method relies on defining an equivalent circuit for the electrolyte, the interface and the sodium in the crack. By choosing suitable values for the resistances, Brennan [6] showed that the current could be partitioned between the crack and the electrolyte thereby leading to a situation in which the crack is fed from the sides as well as at the tip. The approach in this study is to assume that the charge transfer resistance as well as the resistance of sodium is negligible. However, the solution here will be more exact. Further, it is to be noted that the equivalent circuit given by Brennan does not truly represent a crack for the following reason. If one lets the charge transfer resistance and the resistance of sodium in the crack tend simultaneously to zero, the equivalent circuit given by Brennan [6] reduces to a tip fed crack (as assumed by previous investigators) and not to the Laplace solution for the crack problem at hand.

The second objective of this paper is to reemphasize that any realistic model based on Poiseuille pressure must determine crack thickness for the appropriate conditions and that one cannot assume a value of the crack thickness as has been done by some investigators [1, 2, 6]. In view of the strong dependency of critical current density (above which degradation can occur) on crack thickness, an assumed value of crack thickness can always give an apparent agreement with

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experimental results and give a false confidence in the hypotheses on which a given model is based. In fact, one must determine i_{cr} (critical current density) and then examine whether the Poiseuille models are realistic in the present situation. The fallacy in assuming a crack opening displacement can be stated simply by the following. If one were to consider a certain elastic spring of stiffness K and if it were subjected to a force F then the deflection of the spring *cannot* be arbitrarily assumed but is given by F/K. Since the solid electrolyte (β''-alumina) is elastic, the crack thickness cannot be assumed but must be determined based on the pressure, crack length and elastic properties of β''-alumina. Assumption of crack thickness is therefore quite incorrect and can lead to certain misleading conclusions.

Finally, based on the calculations presented here, certain plausible complementary mechanisms for degradation are considered and the role of electrolyte properties in promoting higher cell life is examined.

2. Theoretical analysis

The objective here is to determine the Poiseuille pressure developed inside a crack due to the sodium which is deposited in the crack and which flows towards the open end. As mentioned before, in earlier work, the sodium ions were assumed to be attracted to the tip of the crack and that the crack was therefore not fed from its sides. A more realistic treatment of such a problem must include the solution of the Laplace equation. The analysis presented below assumes that the resistivity of the liquid sodium can be taken to be zero and that the charge transfer resistance (caused for example due to polarization effects) is also zero. In view of the low resistivity of liquid sodium compared to that of β''-alumina, the first assumption is easily justified. The second assumption can be justified if polarization effects are minimal. If polarization effects cannot be neglected, then somehow these must be incorporated. Solution to the Laplace equation in such a case is expected to be very complicated. One may choose an analogue simulation technique and write an equivalent circuit. However, one must be careful to ensure that the chosen equivalent circuit truly represents the problem at hand.

2.1. Statement of the problem

Consider a large plate of some material of resistivity ρ containing a thin crack of length $2l$ as shown in Fig. 1. The crack is filled with some other material whose resistivity is zero. (In practice the resistivity of the material in the crack need not be zero. The field solutions rapidly approach the one for $\rho_{\text{crack}}/\rho_{\text{plate}} = 0$ as long as $\rho_{\text{crack}}/\rho_{\text{plate}} \leqslant 0.05$). A steady state current of density i (amps cm^{-2}) (far away from the crack) passes through the plate as shown in Fig. 1. Since the resistivity in the crack is zero and the current is finite, the potential in the crack is constant, i.e.

$$\Phi(x, 0) = \text{constant}; \quad |x| \leqslant l. \qquad (1)$$

This constant may be chosen to be zero. Further, due to the symmetry about the x-axis, we have

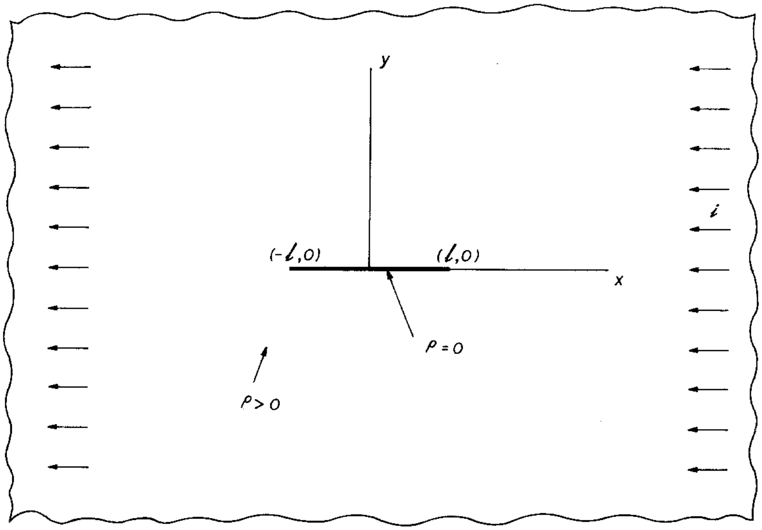

Figure 1 A large plate of some material of resistivity ρ containing a crack of length $2l$ which is filled with a material of $\rho = 0$. i is the uniform steady state current density.

$$\left(\frac{\partial\Phi}{\partial y}\right)(x,0) = 0; \quad |x| > l. \tag{2}$$

Also, as $x \to \pm\infty$, the current density is given by

$$i(x\to\infty, y) = -\sigma\left(\frac{\partial\Phi}{\partial x}\right) = i \tag{3}$$

where σ is the conductivity $(1/\rho)$.

It is well known [7] that mixed boundary value problems of this type can be solved by the appropriate choice of an analytic function $f(z)$ such that

$$f(z) = \Phi + j\psi \tag{4}$$

where $j = (-1)^{1/2}$ and ϕ and ψ are plane harmonic functions. It is easily vertified that the potential $\Phi(x, y)$ can be given by [8]

$$\Phi(x,y) = -j\rho(r_1 r_2)^{1/2}\cos\left(\frac{\theta_1+\theta_2}{2}\right) \tag{5}$$

where

$$r_1 = [(x-l)^2 + y^2]^{1/2}$$

$$r_2 = [(x+l)^2 + y^2]^{1/2}$$

$$\theta_1 = \tan^{-1}\left(\frac{y}{x-l}\right)$$

and

$$\theta_2 = \tan^{-1}\left(\frac{y}{x+l}\right).$$

r_1, r_2, θ_1 and θ_2 are shown schematically in Fig. 2.

For $|x| \leqslant l$ and $y = 0$, note that

$$\theta_1 + \theta_2 = \pm\pi.$$

Thus

$$\Phi(x,0) = 0; \quad |x| \leqslant l. \tag{6}$$

It is also easily verified that

$$\frac{\partial\Phi}{\partial y}(x,0) = 0; \quad |x| > l \tag{7}$$

and that

$$\lim_{x\to\infty}\frac{\partial\Phi}{\partial x} = -i\rho. \tag{8}$$

The amount of current entering the crack (from one face) per unit area between x and $x-dx$ is simply $i(x, 0)$, the local current density, given by

$$i(x,0) = -\sigma\left(\frac{\partial\Phi}{\partial y}\right)(x,0); \quad |x| \leqslant l.$$

$$= \frac{ix}{(l^2-x^2)^{1/2}}. \tag{9}$$

The flux lines and the equipotential lines are shown schematically in Fig. 3. Note that the y-axis $(x = 0)$ is an equipotential line with $\Phi(0, y) = 0$. Let us then consider the half-plane problem of an edge crack of length l filled with sodium such that the wide end opens up into a reservoir of sodium as shown in Fig. 4. The amount of current per unit thickness (in the z-direction) entering between x and $x-dx$ is

$$dI(x,l) = \frac{2ix\,dx}{(l^2-x^2)^{1/2}}. \tag{10}$$

Thus, the amount of current that enters between x and l is given by

$$I(x,l) = 2i\int_x^l \frac{x\,dx}{(l^2-x^2)^{1/2}}$$

$$= 2il\int_{\sin^{-1}(x/l)}^{\pi/2}\sin\alpha\,d\alpha$$

$$I(x,l) = 2i(l^2-x^2)^{1/2}. \tag{11}$$

The pressure drop dp when fluid flows between x and $x-dx$ is

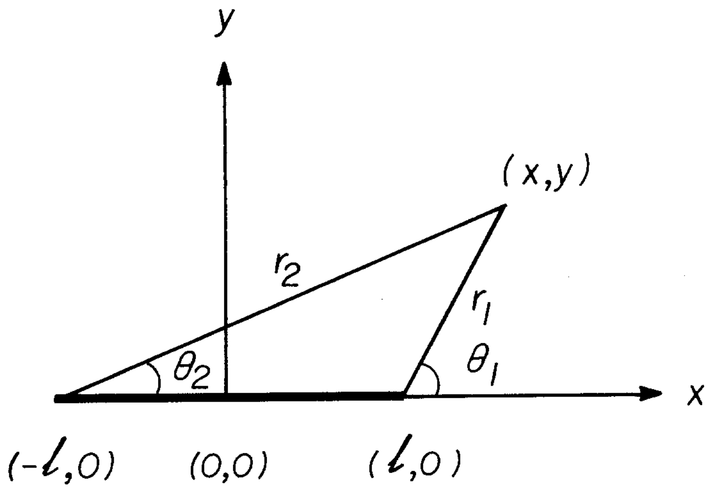

Figure 2 A schematic diagram defining r_1, r_2, θ_1 and θ_2.

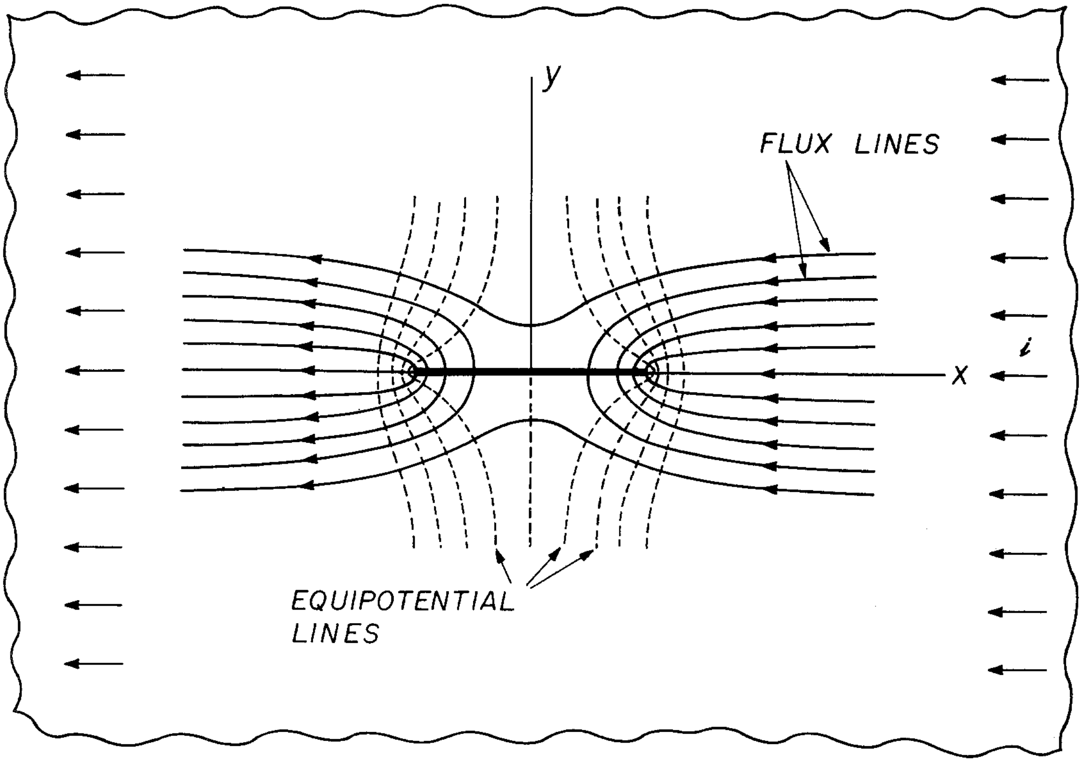

Figure 3 Flux lines and equipotential lines for the problem shown in Fig. 1.

$$\mathrm{d}p = \frac{3}{2}\frac{\eta V_{\mathrm{m}}}{r^3 F} I(x, l)\,\mathrm{d}x \tag{12}$$

in which the Hagen–Poiseuille law has been used for a rectangular channel of thickness $2r$ and width unity. Also, η is the viscosity of sodium, V_{m} is the molar volume of sodium and F is the Faraday constant. Thus

$$\Delta p(x) = p(x) = \frac{3\eta V_{\mathrm{m}} i}{r^3 F}\int_0^x (l^2 - x^2)^{1/2}\,\mathrm{d}x$$

$$p(x) = \frac{3\eta V_{\mathrm{m}} i l^2}{2r^3 F}\left[\sin^{-1}\frac{x}{l} + \frac{x}{l}\left(1 - \frac{x^2}{l^2}\right)^{1/2}\right] \tag{13}$$

and

$$p(l) = \frac{3\pi\eta V_{\mathrm{m}} i l^2}{F r^3}\,. \tag{14}$$

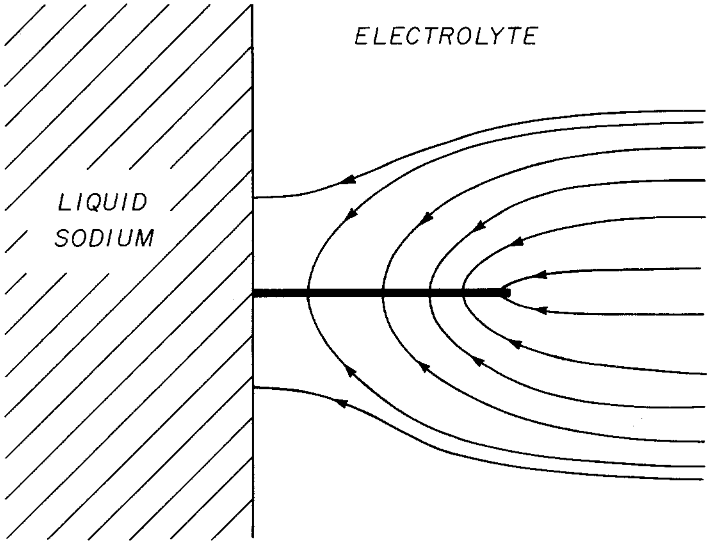

Figure 4 A schematic diagram showing flux lines to a sodium-filled edge crack in β''-alumina during charging.

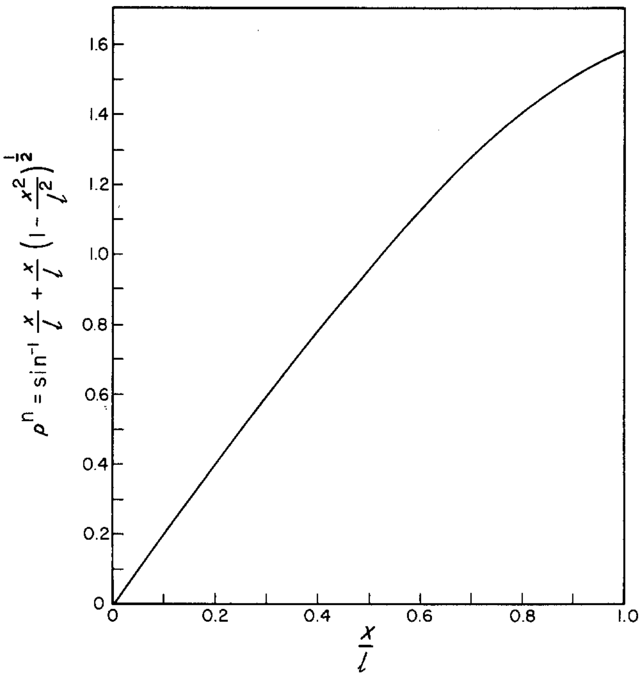

Figure 5 A plot of normalized pressure p^n against x/l.

For a parallel rectangular channel r is independent of x and therefore is out of the integral in the above. But as will be shown later, it is a function of l.

Equation 13 is schematically plotted in Fig. 5. As may easily be seen, the loading created on the crack surfaces is nearly linear (triangular). Equation 14 shows that if the crack has a thickness of $2r$ and if the material is truly rigid (meaning the elastic modulus is mathematically infinite), then $p(l)$ is linearly proportional to i, inversely proportional to r^3 and linearly proportional to l^2. Thus, it deceptively appears as though $p(l)$ should increase with increasing l for a given current density. Some investigators [2, 6] have therefore shown $p(l)$ increasing with increasing l. This however would be true if and only if the elastic modulus is infinite or if the crack opening displacement for zero load is non-zero (and in fact much larger than elastic displacements) such as that created by crack tip blunting due to plastic deformation. Since the elastic modulus is finite, it can in fact be shown that $p(l)$ *decreases* with increasing l. This is demonstrated in the following.

For a plate containing a crack length $2l$ subjected to a uniform pressure p, it can be shown that [9] the crack opens up into an ellipse with plate is πbl which is given by

$$2b = \frac{4\pi(1-\nu^2)}{E}pl. \tag{15}$$

The volume of the crack per unit thickness of the plate is πbl which is given by

$$\pi bl = \frac{2\pi(1-\nu^2)}{E}pl^2 \tag{16}$$

where ν is Poisson's ratio and E is Young's elastic modulus. For an equivalent crack of flat parallel faces that are a distance $2r$ apart, volume per unit thickness is $4rl$. Equating the two volumes

$$4rl = \frac{2\pi(1-\nu^2)}{E}pl^2$$

or

$$r = \frac{\pi}{2}\frac{(1-\nu^2)}{E}pl \tag{17}$$

are obtained.

Sodium deposited in the crack flows towards the open end and the loading created on the crack surfaces is nearly triangular. For an edge crack with linearly increasing loading (triangular loading) along the crack length, it can be shown that [10]

$$r = 0.8982\frac{(1-\nu^2)p(l)l}{E} \tag{18}$$

where $p(l)$ is the value of pressure at $x = l$.

At 300° C $\eta = 3.4 \times 10^{-3}$ poise, $E = 2.07 \times 10^{12}$ dynes cm^{-2}, $\nu = 0.25$ and $V_m = 23.7\,\text{cm}^3\,\text{mol}^{-1}$.

Equation 18 shows that the crack opening displacement (elastic) $2r$ is a function of $p(l)$, l and the elastic constants. Some investigators [2, 6] have assumed r to be an arbitrary adjustable parameter, which is incorrect. Substitution of r from Equation 18 into Equation 14 gives

$$[p(l)]^4 = \left(\frac{3\pi V_\mathrm{m} E^3}{4F(0.8982)^3(1-\nu^2)^3}\right)\left(\frac{\eta i}{l}\right). \quad (19)$$

On substitution for E, V_m, F and η (at 300° C)

$$p(l) = \left(\frac{7.3527 \times 10^7}{l^{1/4}}\right) i^{1/4} \text{ dynes cm}^{-2} \quad (20)$$

is obtained where once again the pressure distribution on the crack surfaces is triangular and Equation 20 gives pressure at $x = l$. Equation 20 shows that the pressure created within the crack is *inversely* proportional to $l^{1/4}$ for a given current density. This result indicates that for a given current density, if the crack length is increased, two opposing factors influence the pressure. The increase in crack length should increase the pressure while increased crack opening displacement should decrease the pressure. It so happens that the latter effect more than offsets the former effect. Within the realms of the theory of elasticity the pressure must decrease with increasing crack length and not increase as given by some investigators [2, 6].

In the above it has been assumed that the crack is a flat parallel slot of thickness $2r$. Crack shape determined previously [4] shows that the crack faces are nearly parallel under triangular loading. It is important to emphasize however, that r has not been assumed to be a constant but it is shown to be a function of $p(l)$ and l. Assumption of constant r (independent of p and l) as made by some investigators [2, 6] cannot be true since it violates the theory of elasticity (except when E is mathematically infinite which implies zero strain for any loading; clearly, this is of no physical significance). Assumption of constant r can only be valid if the crack does not tend to zero thickness for zero pressure and if the corresponding r (for zero pressure) is much larger than the change in crack face displacement (elastic) that would occur when crack faces are subjected to loading. For a crack of length 100 μm under a pressure of 150 MN m^{-2}, the change in crack face displacement is ~ 1000 Å. The crack opening displacement under zero pressure would have to be much greater than 1000 Å such as would occur due to crack tip blunting. Thus, the assumption of fixed r may be justified if say r for zero pressure is at least 10 000 to 15 000 Å. If the cracks are so wide however, the pressure generated within the cracks at any reasonable current density is negligible and the crack would not advance by a microfracture model. Assumption of constant r as made by Richman and Tennenhouse [2] and Brennan [6] is incorrect as well as the further assumption of r of the order of 10 to 50 Å made in [2, 6] in order to obtain critical current densities of the order of 1 to 2 amps cm^{-2}. The objective of any model based on Poiseuille pressure must be to accurately calculate the critical current density so that basic premises of elasticity are not violated. A calculation of critical current density may now be made in light of Equation 20 and the failure criterion; namely the Griffith equation.

We know via the Griffith equation that the critical pressure required to extend the crack is inversely proportional to the square root of the crack length. For triangular loading [10]

$$p_\mathrm{cr} = \left[\frac{E\gamma_\mathrm{eff}}{0.3662(1-\nu^2)l}\right]^{1/2} \quad (21)$$

where p_cr is the value of the pressure at $x = l$ required to extend the crack. With $\gamma_\mathrm{eff} = 10$ J m^{-2}

$$p_\mathrm{cr} = \frac{2.4555 \times 10^8}{l^{1/2}} \text{ dynes cm}^{-2}. \quad (22)$$

For a given crack length and current density, the pressure generated (triangular) is given by Equation 20. The crack would begin to extend when the current density was raised to a value such that $p = p_\mathrm{cr}$. Thus, equating Equations 20 and 22 gives an expression for critical current density, i_cr, given by

$$i_\mathrm{cr} = \frac{1.2439 \times 10^2}{l}. \quad (23)$$

Plots of p and p_cr are shown in Fig. 6. The cross-hatched region is the supercritical region where the crack growth would occur by the Poiseuille pressure model. Equation 20 shows that small changes in either the current density or the crack length has a marginal effect on the pressure developed inside the crack.

3. Discussion

Based on Equation 23 it is tempting to evaluate the critical value of current density above which degradation would occur. For a crack length of 100 μm, the calculated $i_\mathrm{cr} \approx 12\,400$ amps cm^{-2} is clearly an outrageous number. It is important to emphasize that such a high value of i_cr is not the result of any miscalculations; rather it is the true value under the assumptions made in the model.

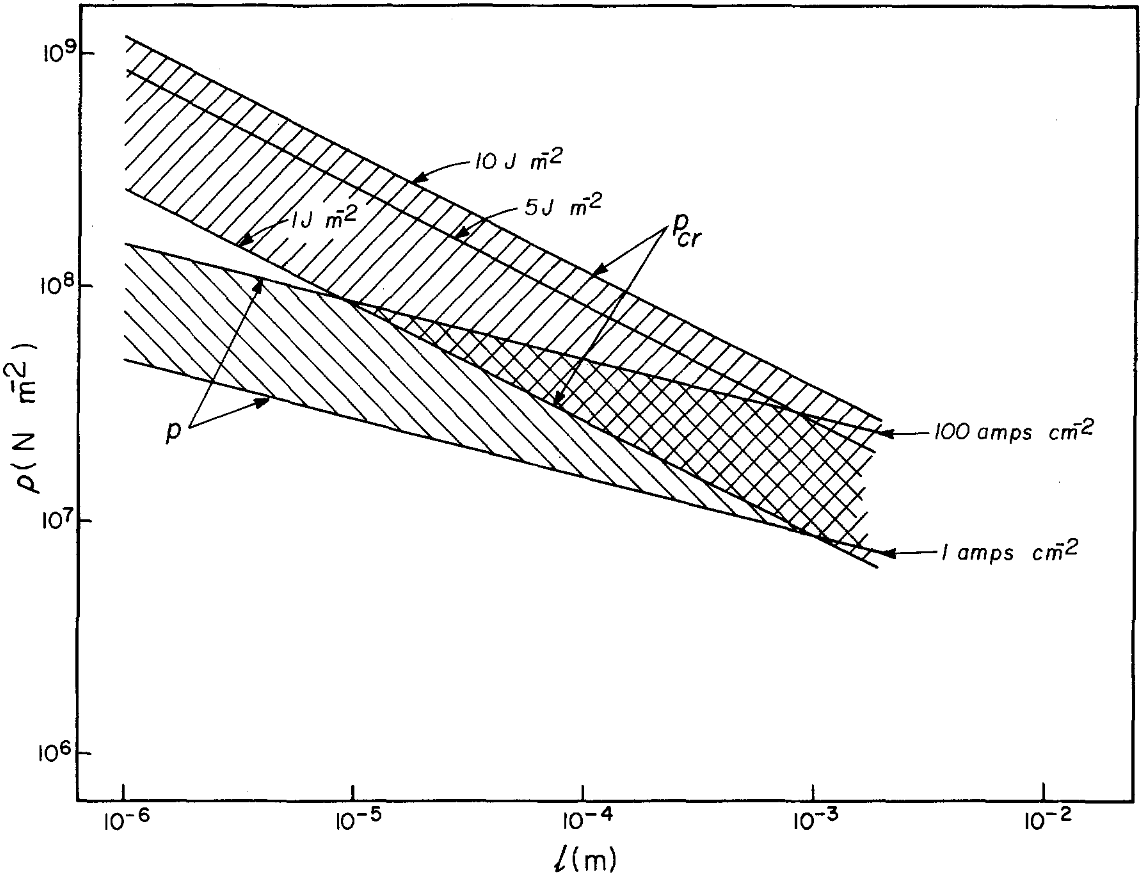

Figure 6 Plots of p against l for $i = 1$ amps cm^{-2} and $i = 100$ amps cm^{-2} and p_{cr} against l for three values of fracture energy. $\gamma_{eff} = 5$ J m^{-2} to $\gamma = 10$ J m^{-2} lines are drawn based on polycrystalline fracture energy while the $\gamma_{eff} = 1$ J m^{-2} line is drawn based on single crystal fracture energy. The cross-hatched region is the supercritical region.

This glaring discrepancy between the theoretical and experimentally observed i_{cr} in fact suggests that there are some other factors of significant importance which have been overlooked if indeed the Poiseuille pressure model is to be a realistic model describing the degradation process adequately. Assumption of arbitrary values of $2r$ as made by some previous investigators [2, 6] simply forces the experiment and theory into apparent agreement and does not explore the applicability of the model to the degradation phenomenon.

There are several factors which could conceivably increase the pressure exerted on the crack faces for a given current density. Since $p \propto i^{1/4}$, small changes in p can make significant changes in i_{cr}. Since the critical value of p for failure to occur is determined by the fracture properties, the factors which could increase p for a given l and i, would drastically lower i_{cr}. Increase in p beyond that given by Equation 20 would mean that p will reach p_{cr} at a lower current density. Some of these factors are given in the following.

(1) The crack surfaces are expected to be rough. Therefore, there will be some head losses as the sodium flows down the crack towards the open end. As the amount of sodium that flows in the crack is determined by the current density and the crack length, the rougher the crack surfaces, the more the pressure will develop.

(2) It is not clear whether the viscosity in very thin cracks (of the order of 1000 Å) would be the same as the viscosity of bulk sodium. Viscosity in thin channels could be greater. In the case of water, it is known that the surface viscosity can be two to three orders of magnitude greater [11]. If the viscosity in thin channels is greater than the viscosity of bulk sodium, then the pressure generated for a given current density and crack length would be greater.

These two factors could raise p beyond that given by Equation 20 and thereby lower i_{cr}.

Previously described current concentration effects can significantly increase current densities at the peripheries on non-wetted areas [12] or at the peripheries of areas across which a large charge transfer resistance exists. Further, local crack propagation may be controlled by the single crystal fracture energy which is about an order of magnitude lower than the polycrystalline fracture energy leading to two orders of magnitude decrease in i_{cr}. Also, there does exist the possibility of a stress-corrosion type of model which may promote crack growth across grain boundaries as originally proposed by Richman and Tennenhouse [2]. The renewed interest in the stress-corrosion model despite negative results regarding stress-corrosion in our earlier experiments [4] is due to the fact that under appropriate conditions liquid sodium completely wets β''-alumina [13] thereby exhibiting chemical affinity.

Finally, there also exists the possibility that internal pores could provide recombination sites where sodium metal could deposit. If cracks are associated with such pores, these could initially propagate* within the electrolyte before opening up on the surface. The rate of crack propagation may then be controlled by the electronic conductivity of β''-alumina. If this is the case then improvement of density may result in improved performance. Impurities which increase electronic conductivity could be detrimental. It is possible that one or all of the above models could explain the degradation of β''-alumina, since, central to all the models is the concept of sodium under pressure in cracks.

One interesting consequence of the Poiseuille pressure model is that the amount of sodium flowing out of the open end of the crack, at the condition of criticality, is independent of crack length. This is shown in the following. From Equation 14 it is known that

$$p = \frac{3\pi\eta V_m i l^2}{4Fr^3} \tag{14}$$

where r is not a constant but is given by

$$r = \frac{\pi(1-\nu^2)}{2E} pl. \tag{17}$$

The volume flow rate of sodium exiting from the open end is given by

$$\dot{V}_{out} = \frac{2rp(2r)^2}{12\eta l} \tag{24}$$

for unit width of the crack. At the condition of criticality, the above reduces to

$$\dot{V}_{out} = \frac{\pi^3}{3}\left[\frac{(1-\nu^2)\gamma_{eff}}{\eta E}\right] \tag{25}$$

which is independent of crack length. The amount of sodium that enters the crack per unit time on the other hand is linearly proportional to the crack length. Thus, the model would predict that the crack would accelerate [4] since the difference $(\dot{V}_{in} - \dot{V}_{out})$ is taken up by the increased crack volume. Experimental observation has, however, shown that the rate of crack propagation (dendrite penetration) is nearly constant at constant current density. This implies that $\dot{V}_{in} \propto l^{1/2}$ (because the critical volume of the crack is proportional to $l^{3/2}$; thus the rate of change of crack volume is proportional to $l^{1/2}$). However, if steady state ion focussing is established then $\dot{V}_{in} \propto l$. This implies that during the crack propagation stage, the steady state ion focussing is not maintained and one must consider the transient problem of diffusion of sodium ions towards the crack.

4. Conclusions

(1) The flow of sodium ions to a sodium-filled crack has been determined via a solution to the Laplace equation.

(2) For a given current density, the pressure drop (from the tip to the open end) *decreases* with increasing crack length.

(3) Very high values of i_{cr} calculated suggest that there are other factors which tend to increase p for a given current density. Several experimental results tend to support the Poiseuille model, however, Perhaps, a detailed calculation of pressure drop in thin channels would be required for reasonable calculation of i_{cr}. A calculated value of i_{cr} in the neighbourhood of 100 amps cm^{-2} would be reasonable in the light of the current concentration near non-wetted areas discussed previously.

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*Provided an electronic short exists between the pore and the sodium reservoir.

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