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The role of superimposed stresses on the degradation of solid electrolytes

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The role of externally applied stresses on solid electrolyte breakdown under electrolytic conditions is examined. It is shown that both applied compressive as well as tensile stresses when incorporated into the Poiseuille pressure model enhance the propensity to failure, consistent with experimental observations. Implications regarding the use of transformation toughened solid electrolytes in electrochemical systems are discussed. It is further demonstrated that the electrolyte breakdown by the supersaturation of ions recently proposed is incorrect.

1. Introduction

It has been known for some time that nonprotonic cationic solid electrolytes undergo degradation during electrolysis above some threshold or critical current density. This degradation manifests itself in the form of dendritic or filamental growth which originates from the ion neutralization surface. This phenomenon has been modelled by several researchers [1–5] based on the concept that a hydrodynamic pressure developed by the flowing fluid exerts stresses on the crack surfaces which cause the crack to extend. Experimental results have been presented [6, 7] which support the hypothesis. Theoretical calculations were based primarily on the assumption of a two-dimensional crack despite the true three-dimensional nature of the crack problem. A lack of quantitative agreement between the measured and the calculated critical current density, i_{cr}, despite the fact that qualitative features of degradation were entirely consistent with the concept of degradation by fluid pressure (Poiseuille pressure), was attributed to the over simplification of the problem as a two-dimensional crack problem. Subsequently, Virkar and Viswanathan [8] semiquantitatively analysed the three-dimensional filament problem and showed good quantitative agreement between theory and experiment. The results of their analysis indicated that

$$i_{cr} = \frac{AK_c^4}{\eta}\frac{c^2}{l^3} \qquad (1)$$

where K_c is the fracture toughness, η the viscosity of sodium, $2c$ the width of the filament, l the length of the filament and A a constant containing elastic constants.

This analysis (as well as prior analyses [3, 4]) indicates that increasing K_c would have a beneficial effect on the resistance to degradation. In subsequent works [9, 10], it was demonstrated that toughening of β''-alumina can be effected by incorporating zirconia and that the critical current density can indeed be increased [11]. It is well known that if a transformation toughened ceramic is surface ground, compressive stresses are developed due to the tetragonal $ZrO_2 \rightarrow$ monoclinic ZrO_2 transformation in the near-surface region. It is of interest, therefore, to determine what role, if any, would such stresses play in the degradation of Na–β''-alumina electrolytes. Other sources of residual stresses include thermal mismatch between mating components near a seal. In a sodium–sulphur battery, the seal in question is the α-alumina header/β''-alumina electrolyte seal.

Recently, Kuribayashi and Nicholson [12] conducted electrolytic degradation studies on β''-alumina and Nasicon notched beam samples with both tensile and compressive superimposed stresses. Their results indicated that degradation enhanced under both tensile and compressive stresses. The fact that compressive stresses enhanced the degradation was assumed by Kuribayashi and Nicholson [12] as an obvious contradiction to the Poiseuille pressure model. They further presented another model for degradation [12, 13] which, however, does not account for a vast body of data on degradation. The purpose of this paper is to demonstrate that the Poiseuille pressure model self consistently explains their data. The erroneous conclusions reached by Kuribayashi and Nicholson [12] are the result of not taking into account the role of external stresses in the case where the pressure of the flowing fluid is affected by the external stresses. In short, the shape and the size of crack-opening determines the pressure and pressure in turn determines the shape and the size of the crack-opening displacement.

2. Analysis

2.1. Crack growth under external compression

Fig. 1a shows a schematic of the experimental arrangement used by Kuribayashi and Nicholson [12]. The presence of a notch provides a site for stress concentration with the result that the compressive stress varies schematically as shown in Fig. 1b. Thus, a crack emanating from the root of the notch experiences a greater closure stress at the open end (A) than at the tip (B). To understand how this stress will enhance degradation, let us examine the following analogy.

Fig. 2a shows a plastic tube of diameter, d, and

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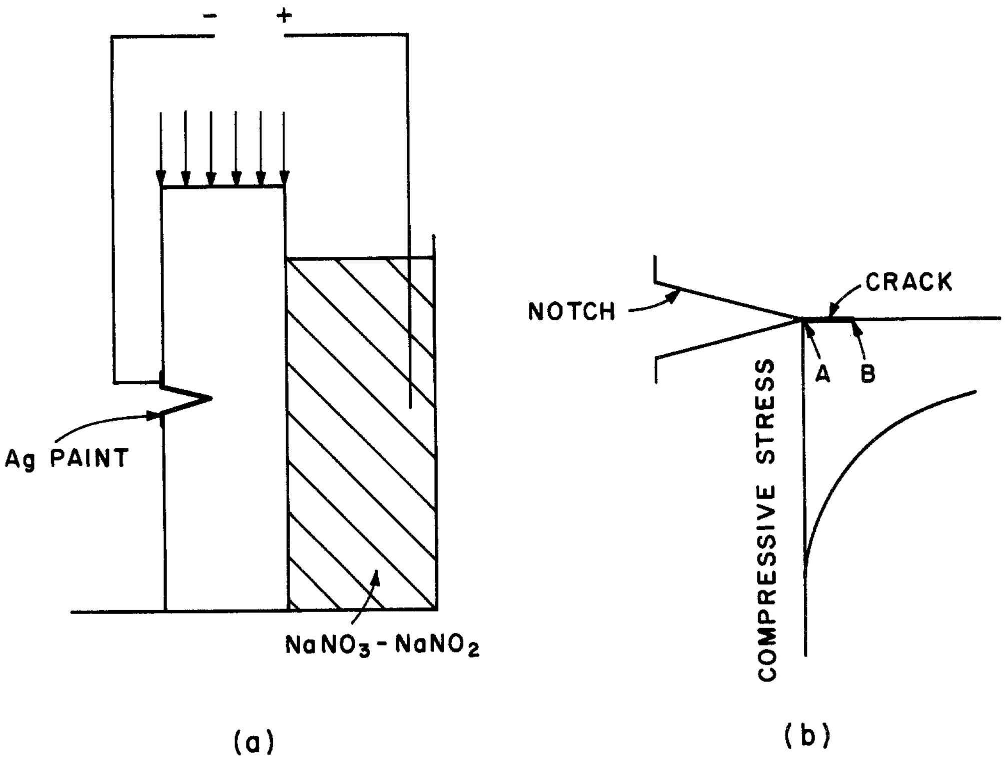

Figure 1 (a) A schematic of the experimental arrangement used by Kuribayashi and Nicholson [12]. (b) A schematic showing stress distribution just ahead of the machined notch. AB denotes a small crack emanating from the root of the notch.

length, L, through which a fluid flows at a constant flow rate of $\dot{V}$ (cm^3 sec^{-1}). The tube contains a crack of depth, c, at the right end. The local hydrodynamic pressure will act on the crack surface and if the stress intensity factor, K, exceeds the critical stress intensity factor, K_c, then the crack will extend thereby rupturing the tube. Fig. 2b shows an identical tube with the same rate of fluid flow passing through the tube except that the tube is partially pinched off at that left end. Clearly, the pressure head drop from the right end to the left end for the same flow rate is greater for the case shown in Fig. 2b. That is, the corresponding pressure exterted on the crack surface in Fig. 2b is greater. Thus, for a given flow rate, the stress intensity factor is greater in Fig. 2b than in 2a and the crack in Fig. 2b may extend but that in Fig. 2a may not. The net effect is that by applying compression, we have increased the probability of tube failure. The solid electrolyte degradation problem in the Poiseuille model is very similar to the one discussed here. When the overall current density is maintained constant, as in the experiments of Kuribayashi and Nicholson [12], the volume flow rate of sodium for a given crack length, l, is fixed.

With reference to degradation of solid electrolytes by the Poiseuille pressure model, let us assume the

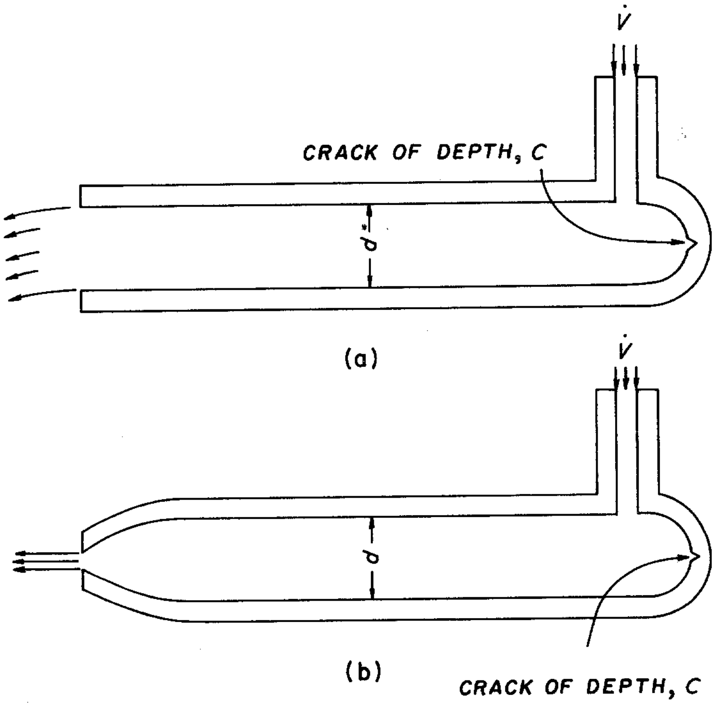

Figure 2 (a) A tube of diameter d, and length l through which a fluid flows at a constant rate of $\dot{V}$ (cm^3 sec^{-1}). The tube contains a crack of depth c. (b) An identical tube as in Fig. 2a with the same rate of fluid flow, except that the tube is partially pinched off at the exit end.

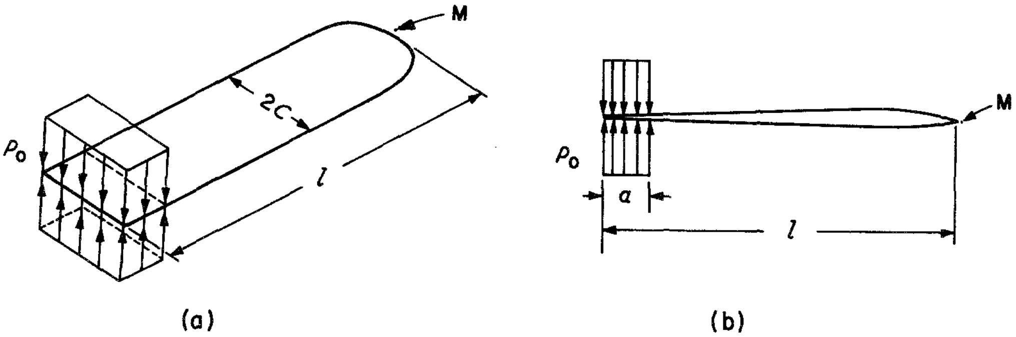

Figure 3 (a) A schematic showing a crack of width, $2c$, and length, l through fluid flows. The fluid enters in the region near M and exits at the left end. Also superimposed is external compression of magnitude p_0 over part of the length. (b) Side view of the crack shown in Fig. 3a.

crack to be in the form of a thin ribbon of width $2c$ and length l with its tip being circular with radius c [8] (see Fig. 3). Consider the case where a compression (pressure) of the amount p_0 (positive value) is applied over some distance from the surface. As long as the distance $a \ll l$, stress at M due to this p_0 is nearly zero by the Saint Venant's principle. The pressure has the effect of closing the crack. For a given current density, i, the volume flow rate is given by

$$\dot{V} = \frac{i\pi l^2 V_m}{F} \qquad (2)$$

where V_m is the molar volume of sodium and F the Faraday constant.

Following Virkar and Viswanathan [8], the pressure distribution in the absence of compressive stresses is given by*

$$p^0(y) = 2\left[\frac{\eta V_m i E^3 l^2}{(1-\nu^2)^3 F c^4}\right]^{1/4} y^{1/4} \qquad (3)$$

which is shown schematically in Fig. 4. In Equation 3, E and ν denote Young's modulus of elasticity and Poisson's ratio, respectively. When the externally applied pressure, p_0, acts over some distance, a, which tends to close the crack, the pressure developed within the fluid must act in an opposing manner to ensure that the crack remains open. Thus, the pressure in the fluid near the open end (i.e. for $y < a$) will be given by

$$p'(y) \simeq p^0(y) + p_0 \qquad (4)$$

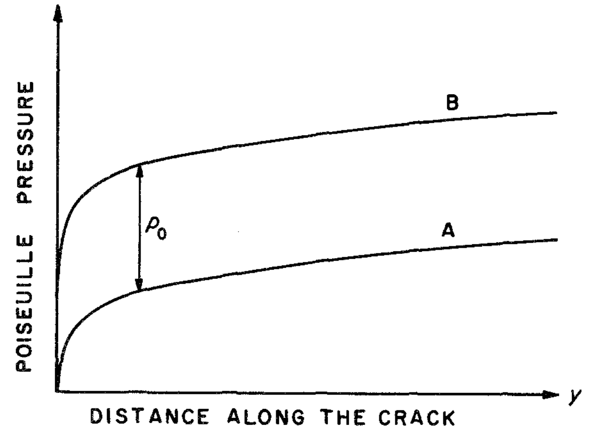

Figure 4 A schematic of Poiseuille pressure variation along the length of the crack. (A) Without external stress (B) with external compression acting over part of the crack as shown in Fig. 3. Near the tip of the crack (right end), the pressure will rise more rapidly than shown here because the crack width narrows near the tip (Fig. 3b). This leads to enhancement of K near M compared to anywhere along the crack front.

Assuming that the pressure profile in the fluid is simply displaced by the amount p_0 as shown in Fig. 4, one can approximate the pressure at y by

$$p'(y) \simeq p_0 + 2\left[\frac{\eta V_m E^3 l^2 i}{(1-\nu^2)^3 F c^4}\right]^{1/4} y^{1/4} \qquad (5)$$

Since we have assumed the local crack opening displacement to be given by the two-dimensional problem of an elliptical crack [8], the above analysis leads to one unrealistic feature, namely that the crack profile abruptly changes at $y = a$. This, of course, is not true. The profile will be smooth. The objective of the analysis is to simply show that the pressure at any y increases due to compression over part of the crack. The relations developed here are therefore approximate.

Now when $p(l) \geq p_{cr}$, failure occurs.

Thus,

$$p'(l) = p_{cr} = \frac{\alpha K_c}{c^{1/2}} \simeq p_0 + 2\left[\frac{\eta V_m E^3 l^3}{(1-\nu^2)^3 F c^4}\right]^{1/4} (i_{cr})^{1/4} \qquad (6)$$

where α is the appropriate geometric constant, or

$$i_{cr} \simeq \frac{(1-\nu^2)^3 F c^4}{16\eta V_m E^3 l^3}\left(\frac{\alpha K_c}{c^{1/2}} - p_0\right)^4 \qquad (7a)$$

or

$$i_{cr} \simeq i_{cr}(0)\left(1 - \frac{p_0 c^{1/2}}{\alpha K_c}\right)^4 \qquad (7b)$$

which shows that the presence of compressive stress over part of the crack decreases the critical current density. The semiquantitative analysis presented here tacitly assumes that the pressure p_0 acts over a sufficient distance a to ensure that the crack remains nearly closed at its open end. Furthermore, rigorous analysis should lead to some dependency of i_{cr} on a. The purpose of the calculation is to simply show an order of magnitude effect of compressive stresses on i_{cr}.

The analysis can be easily extended to the case of uniform external pressure acting over the entire length

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*There are a few typographical errors in reference [8]. Also, in Equation 11a of [8], i_{cr} is in $\mathrm{A\,cm^{-2}}$ when c and l are in μm, not cm.

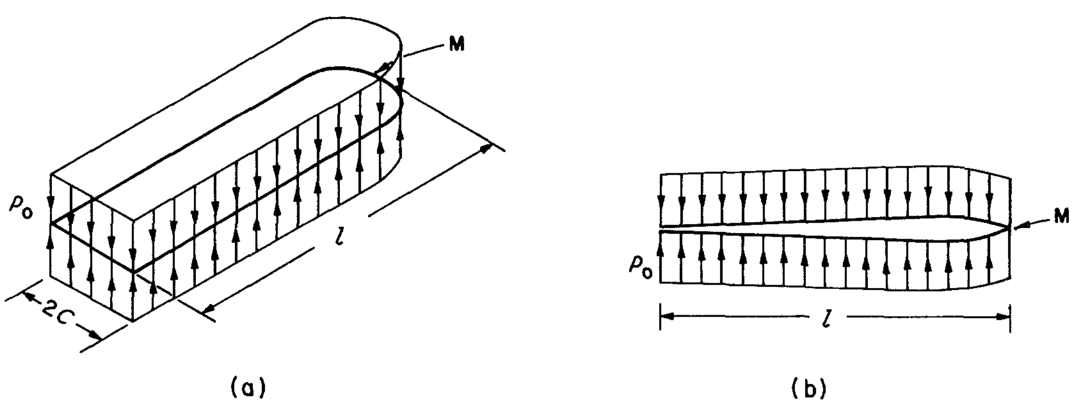

Figure 5 (a) A schematic of the crack as in Fig. 3a but with external compression acting over the entire length of the crack. (b) Side view of the crack shown in Fig. 5a.

(see Fig. 5). The local crack opening displacement is given by [8]

$$b(y) = \frac{(1-\nu^2)c}{E}[p'(y) - p_0] \tag{8}$$

and the pressure drop in the fluid between y and $y - \mathrm{d}y$ is given by

$$\mathrm{d}p'(y) = \frac{4\eta V_{\mathrm{m}} i l^3 E^3 \mathrm{d}y}{(1-\nu^2)^3 F c^4 [p'(y) - p_0]^3} \tag{9}$$

or

$$\int_{p_0}^{p'(l)} [p'(y) - p_0]^3 \,\mathrm{d}p'(y) = \frac{4\eta E^3 V_{\mathrm{m}} l^3 i}{(1-\nu^2)^3 F c^4} \tag{10}$$

The lower limit is $p'(0) = p_0$ which gives the local crack displacement to be zero, the lowest possible value. Integration gives

$$p'(l) - p_0 = 2\left[\frac{\eta V_{\mathrm{m}} i E^3 l^3}{(1-\nu^2)^3 F c^4}\right]^{1/4} \tag{11}$$

For failure to occur[†] $p'(l) - p_0 \geqslant p_{\mathrm{cr}} = \alpha K_{\mathrm{c}}/c^{1/2}$. Thus

$$i_{\mathrm{cr}} = \frac{(1-\nu^2)^3 \alpha^4 K_{\mathrm{c}}^4 F}{16\eta V_{\mathrm{m}} E^3} \frac{c^2}{l^3} \tag{12}$$

which is simply equal to $i_{\mathrm{cr}}(0)$ in the absence of any external compressive stress.

We thus come to the following conclusion: the critical current density, i_{cr}, for the onset of degradation would either remain approximately[‡] unaltered or would decrease under external compressive stress depending upon whenther the stress applied is uniform or nonuniform. It is easily seen that the experimental arrangement of Kuribayashi and Nicholson [12] leads to a nonuniform compressive stress on the crack and therefore degradation was enhanced under a compressive stress.

2.2. Crack growth under external tension

Consider a uniform tension of magnitude p_0 applied over the entire length of the filament (crack). The local crack opening displacement is now given by [8]

$$b(y) = \frac{(1-\nu^2)c}{E}[p'(y) + p_0] \tag{13}$$

and the Poiseuille law becomes

$$\mathrm{d}p'(y) = \frac{4\eta V_{\mathrm{m}} i l^2 E^3}{(1-\nu^2)^3 F c^4 [p'(y) + p_0]^3} \mathrm{d}y \tag{14}$$

Thus

$$\int_0^{p'(l)} [p'(y) + p_0]^3 \,\mathrm{d}p'(y) = \frac{4\eta E^3 V_{\mathrm{m}} l^3 i}{(1-\nu^2)^3 F c^4} \tag{15}$$

which upon integration gives

$$[p'(l) + p_0]^4 = \frac{16\eta V_{\mathrm{m}} i E^3 l^3}{(1-\nu^2)^3 F c^4} + p_0^4 \tag{16}$$

The condition of criticality will be given by

$$p'(l) + p_0 \geqslant p_{\mathrm{cr}} = \frac{\alpha K_{\mathrm{c}}}{c^{1/2}} \tag{17}$$

Thus

$$\frac{16\eta V_{\mathrm{m}} E^3 l^3}{(1-\nu^2)^3 F c^4} i_{\mathrm{cr}} + p_0^4 \geqslant \frac{\alpha^4 K_{\mathrm{c}}^4}{c^2} \tag{18}$$

which gives

$$i_{\mathrm{cr}} = \frac{(1-\nu^2)^3 F \alpha^4 K_{\mathrm{c}}^4}{16\eta V_{\mathrm{m}} E^3} \frac{c^2}{l^3}\left(1 - \frac{c^2 p_0^4}{\alpha^4 K_{\mathrm{c}}^4}\right) \tag{19}$$

or

$$i_{\mathrm{cr}} = i_{\mathrm{cr}}(0)\left(1 - \frac{c^2 p_0^4}{\alpha^4 K_{\mathrm{c}}^4}\right) \tag{20}$$

Equation 20 shows that external uniform tension, p_0, will decrease the critical current density for the onset of degradation. For

$$p_0 \geqslant \frac{\alpha K_{\mathrm{c}}}{c^{1/2}}, \qquad \text{the } i_{\mathrm{cr}} = 0.$$

i.e. the externally applied tension will cause failure of the electrolyte without the necessity to pass any current. With reference to Equation 20, once again, it is to be emphasized that it is assumed that K reaches K_{c} at M before anywhere along the crack front. This is not true, however, for reasons pointed out by Bansal [14]. Thus, above some p_0, K will reach K_{c} along the long edges of the filament and the crack will extend laterally. In any event, Equation 18 does indicate that degradation will be enhanced under an applied uniform tension.

[†] Here, once again, we have assumed that the stress intensity factor at M is greater than anywhere near the crack front. This may not be the case with increasing p_0 and crack may extend laterally for large values of p_0.

[‡] Approximately because of the assumptions made regarding crack opening displacements.

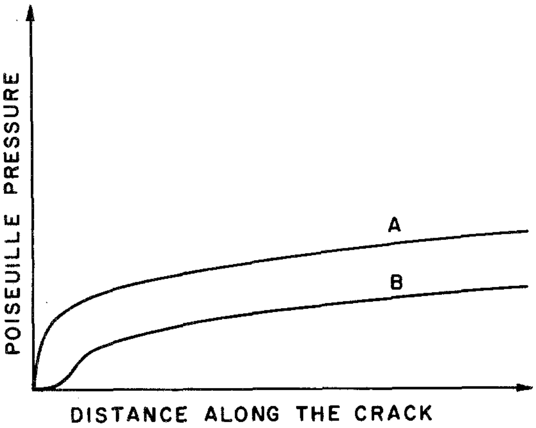

Figure 6 A schematic of Poiseuille pressure variation along the length of the crack. (A) Without external stress (B) with external tension acting over part of the crack.

(If, however, one applies external tension near the open end of the filament, intuitively, one would expect a slight increase in i_{cr}. This is so because the pressure distribution will be somewhat lower than in the case with no applied stress as shown in Fig. 6. However, it is assumed that K does not exceed K_c near the open end or else crack will extend laterally.)

The important conclusion is that externally applied tension would decrease i_{cr} i.e. would increase the propensity to degradation.

The analysis presented here, therefore, shows that degradation will be enhanced under both applied tension as well as compression. This is precisely what Kuribayashi and Nicholson [12] observed. The results of Kuribayashi and Nicholson [12] are therefore in complete accord with the expectations of the Poiseuille pressure model. Erroneous conclusions reached by Kuribayashi and Nicholson [12] are the result of not taking into account the fact that externally applied stresses do affect the crack opening displacement which in turn affects the Poiseuille pressure generated for a given current density.

3. Discussion

With the aid of Equation 7, it is instructive to estimate the reduction in i_{cr} upon the application of compressive stresses on part of the crack. Let us choose $2c \simeq 60\,\mu\text{m}$, $\alpha \simeq \pi^{1/2}/2$ of a penny-shaped crack, and $K_c \simeq 2\,\text{MPa}\,\text{m}^{1/2}$. Then for $p_0 \simeq 150\,\text{MPa}$, we obtain $i_{cr}/i_{cr}(0) \simeq 0.29$. $i_{cr}(0)$ is calculated to be $7.7\,\text{A}\,\text{cm}^{-2}$. Thus, under compression of 150 MPa, i_{cr} reduces to $2.23\,\text{A}\,\text{cm}^{-2}$. That is, the critical current density is significantly reduced by compressive stresses acting over part of the length. Based on Equation 7, if $p_0 c^{1/2}/\alpha K_c \geqslant 1$, then $i_{cr} \simeq 0$. The implication is that the crack closure pressure is of a sufficient magnitude to ensure that K will exceed K_c before the open end opens up to let the incoming sodium out. This problem is conceptually similar to that of a crack contained in an ion exchanged glass with surface compressive stresses. For a crack which is deeper than the zone of compression, K can reach K_c even when the crack surfaces at the open end are in contact with each other [15]. In such a case, the crack will extend and no sodium will flow out into the reservoir. (It is assumed, of course, that a thin sodium filament exists which is electrically connected to the reservoir to provide electronic path). It is interesting to note that Kuribayashi and Nicholson [12] observed significant enhancement in degradation at 75 MPa compression at $1\,\text{A}\,\text{cm}^{-2}$ while little or no degradation occurred at $1.5\,\text{A}\,\text{cm}^{-2}$ without any compression.

Our calculations further indicate that if the compressive stress acts uniformly over the entire crack, the critical current density is unaffected. From a practical standpoint, the significance of this relates to transformation toughening. It is well known that if transformation toughened ceramics are surface ground, a layer of compressive stress develops which is formed due to the tetragonal → monoclinic transformation in zirconia. This layer is typically a few micrometres in depth. Recently, it has been demonstrated that β''-alumina can be transformation toughened [9, 10] and that the critical current density for the onset of degradation is indeed enhanced [11]. The enhancement in i_{cr}, although substantial, (three times that of untoughened β'-alumina), was lower than predicted. The samples used in this study [11] were subjected to a drilling operation thereby inducing surface compressive stresses. The analysis presented here would indicate that if the initial crack is deeper than the region of compressive stresses, the critical current density will be lower as given by Equation 7. Thus, in transformation toughened β''-alumina there are two factors which influence i_{cr}. Increase in K_c increases $i_{cr}(0)$ as given by Equation 1. A layer of compressive stress decreases i_{cr} as given by Equaton 7. Literature on transformation toughened ceramics shows that the depth of compression is about $10\,\mu\text{m}$ which is much smaller than the typical flaw depths which are several times larger. From a practical standpoint then, it is essential to ensure that the toughened β''-alumina is not surface ground so that a surface compressive layer does not exist. If it is surface ground, it may be necessary to ensure that the depth of compression is large enough to entirely contain a typical surface flaw.

The other source of nonuniform stresses is due to thermal mismatch between mating parts. Conventional wisdom would dictate that as long as β''-alumina tube is under compression, the tube will be less likely to fail. Our analysis of the Poiseuille pressure model shows that this may not be the case. In fact, nonuniform compression could be detrimental. One should thus strive to build a seal in such a way that no stresses, either tensile or compressive are generated in the solid electrolyte. The analysis pertaining to the externally applied tensile stresses is self explanatory and further discussion of it is not warranted except to point out that when the experiments are conducted in open air, which was the case in the experiments of Kuribayashi and Nicholson [12], moisture assisted subcritical crack growth can also occur. As to how much of the crack growth in their experiments was moisture assisted is difficult to evaluate.

With reference to the dependence of critical current density on temperature, it appears that there is some confusion [12] regarding the predictions of the Poiseuille model. Specifically, Equation 1 demonstrates that the onset of crack growth will occur at a higher current density at higher temperatures due to the fact that viscosity of sodium decreases with increasing temperature. This has been amply demonstrated [6, 7]. Specifically, it has been shown that Na/Na cells degrade at 1 A cm^{-2} at 120° C in a matter of minutes, yet last indefinitely at 4 A cm^{-2} at 350° C without any signs of degradation. Results of Hunt *et al.* [16] also indicate that very high current densities (15 A cm^{-2}) can be passed without failure at higher temperatures. In the study of Kuribayashi and Nicholson [12], the kinetics of crack growth measured was found to be thermally activated with activation energy that is about the same as for ionic conduction. Equation 2 does not address the subsequent crack growth kinetics. However, Viswanathan and Virkar [17, 18] have addressed the question of the kinetics of crack growth. Specifically, it was shown that as the crack advances, the flux of sodium ions arriving towards it is no longer steady state since the interface between sodium and β''-alumina is not perfectly reversible [19]. As such, the interfacial capacity must be charged as the crack continues to advance. In short, the flux consists of two terms: the ohmic current and the displacement current. The displacement current does not lead to the formation of sodium metal. The relaxation time for the phenomenon was shown to depend upon the ionic conductivity. The main conclusion was that the kinetics of crack growth will increase with increasing temperature. This was demonstrated experimentally [17]. Furthermore, experiments on Ag–β''-alumina and Na–β''-alumina showed, as expected, that the rate of crack growth was higher in Na–β''-alumina on account of its higher conductivity. Therefore, the results of Kuribayashi and Nicholson [12] are entirely consistent with the Poiseuille pressure model.

Finally, we will point out one principal error in the qualitative model presented by Nicholson [13] which raises some questions regarding the validity of his model. Specifically, Nicholson [13] proposes that more sodium ions arrive at certain sites within β''-alumina near the crack tip than are discharged. The argument relates to the diffusion distance as calculated using the diffusivity of Na-ion and time. This presumably leads to the precipitation of sodium[§] and collapse of the lattice. It must be recognized that the flux of ionic species occurs down an electrochemical potential gradient and not down a chemical potential gradient. In fact, even after application of an electric field, the concentration of Na-ions everywhere within the electrolyte is essentially unchanged. The predominant term in electrochemical potential is the local electrostatic potential multiplied by the ionic charge. Thus, the super-saturation Nicholson [13] proposes cannot occur. That is, the increase in electrostatic potential will stop further influx of Na-ions in a given region in order to preserve local electroneutrality [22]. It is well known that ionic fluxes are formulated with the basic premise that the local electroneutrality is maintained [22–25].

Experimentally, the model proposed by Nicholson [13] does not explain one important observation; namely, that the critical current density increases by orders of magnitude just above the melting point of sodium [6]. It has been observed that the i_{cr} below the melting point of sodium is in the range of mA cm^{-2} consistent with high viscosity of solid sodium, while above the melting point the i_{cr} is in the range of a few A cm^{-2} consistent with its much lower viscosity. Since sodium is very soft as a solid, it is quite proper to speak in terms of its viscosity. In fact, our experiments [26] show that in the case of Ag–β''-alumina, current density on the order of 50 μA cm^{-2} can be passed for over a month at 900° C (m.p. of silver is 960° C) without failure. But if the current density is raised above about 100 μA cm^{-2}, dendritic growth instantaneously occurs. The model by Nicholson [13] does not predict an abrupt change in propensity to degradation just below and above the melting point of sodium in the case of degradation of Na–β''-alumina.

Further inconsistency of Nicholson's [13] argument lies in the explanation of the effect of compression and tension on degradation. Nicholson [13] suggests that applied compressive stress will lead to precipitation of sodium on planes parallel to the loading axis while applied tension will lead to the precipitation of sodium on planes perpendicular to the loading axis. However, the state of stress just ahead of the crack in plane strain is that of hydrostatic tension or compression depending upon whether the load applied is tensile or compressive [27]. As such, if stress assisted precipitation of sodium occurs under tensile loading, dissolution must occur under compressive loading.

4. Conclusions

Based on this work, the following conclusions can be drawn.

1. Externally applied compression as well as tension enhances the propensity to failure by the Poiseuille pressure model. The data of Kuribayashi and Nicholson [12] are in complete accord with the Poiseuille pressure model.
2. Supersaturation of Na-ions cannot occur as described by Nicholson [13] since the electrostatic potential term in the electrochemical potential was not accounted for.

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[§] Internal precipitation of sodium can occur but not as proposed by Nicholson [13]. It can occur provided there is a local variation in electronic conductivity as shown by DeJonghe [20]. The kinetics of precipitation and pressurization and its relation to degradation has been addressed by Virkar [21].

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