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SOLID ELECTROLYTE DEGRADATION WITH APPLIED STRESS

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In a recent paper Kuribayashi and Nicholson [1] reported some results on the effects of an applied mechanical stress on the current density at which electrolytic degradation started for sodium beta"-alumina and Nasicon solid electrolytes. Both compressive and tensile stresses were reported to lead to a **decrease** in the observed critical current density for onset of degradation by crack propagation. The results are remarkable, since they do not agree with what is to be expected when combined mechanical and electrolytic stresses are considered. In the present note we show that applied tensile stresses should **reduce** the critical current density for failure initiation, while compressive stresses should cause an **increase**.

When solid electrolyte degradation is due to Poiseuille pressure, generated by the electrolytic deposition of metallic sodium inside a pre-existing surface flaw, [2-4] an applied mechanical stress would affect the degradation process in two ways. First, it will change the width of the crack, thereby changing the Poiseuille pressure. Second,

it will contribute to the stress intensity at the crack tip. An analysis of the degradation process whereby a pre-existing elliptical-cylindrical crack is propagated under the influence of the electrolysis-generated Poiseuille pressure [3] leads to an expression for the intensity at the crack tip of the form:

$$K_I^P = \alpha\delta^{-3} j_\infty$$

where α is constant for constant crack length and is dependent on the viscosity of the sodium. is the crack opening displacement, and j_∞ is the macroscopic current density. We will assume here that, to a first approximation, the crack shape is independent of the source of the stress, and remains elliptical. The total stress intensity factor, K_I, is then dependent on the crack opening displacement, δ, only, and crack propagation will occur at the critical crack opening displacement, δ_c. The total stress intensity factor at criticality, K_{IC}, can then be expressed as

$$K_{IC} = K_I^P + K_I^\sigma \qquad \text{Eqn. 1}$$

or

$$1 = K_I^P / K_{IC} + K_I^\sigma / K_{IC} \qquad \text{Eqn. 2}$$

where K_I^P is the component of K_I due to the electrical current, and K_I^σ is the component due to the applied mechanical stress. Since

$$K_{IC} = \alpha\, \delta_c^{-3}\, j_c\,(o) = \sigma_c \beta \qquad \text{Eqn. 3}$$

where j_c (0) is the critical current density at σ =0, σ_c is the

critical mechanical stress at $j_\infty = 0$, and β is a constant,[5] Eqns. 1-3 yield for the critical current in the presence of a stress, $j_c(\sigma)$

$$j_c(\sigma)/j_c(o) = 1 - \sigma/\sigma_c \qquad \text{Eqn. 4}$$

Eqn. 4 clearly shows that the critical current for failure initiation is linearly dependent on the applied stress. The disagreement of the observations of Kuribayashi and Nicholson from this prediction would require significant deviations from the postulates on which the derivation is based. It is, at present, not evident how such deviations should arise.

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References

[1] K. Kuribayashi and P. S. Nicholson, J. Mat. Sci., 18 (1983) 1590.

[2] R. D. armstrong, T. Dickinson, and J. Turner, Electrochem. Acta 19 (1974 517.

[3] L. A. Feldman, and L. C. De Jonghe, J. Mat. Sci., 17 (1982) 517.

[4] A. Virkar and L. Vismanatan, J. Mat. Sci., 18 (1983) 1202.

[5] H. Tada, P. Paris, and G. Irwin, "The Stress Analysis of Cracks Handbook", Del Research Corp., St. Louis, Missoure.

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