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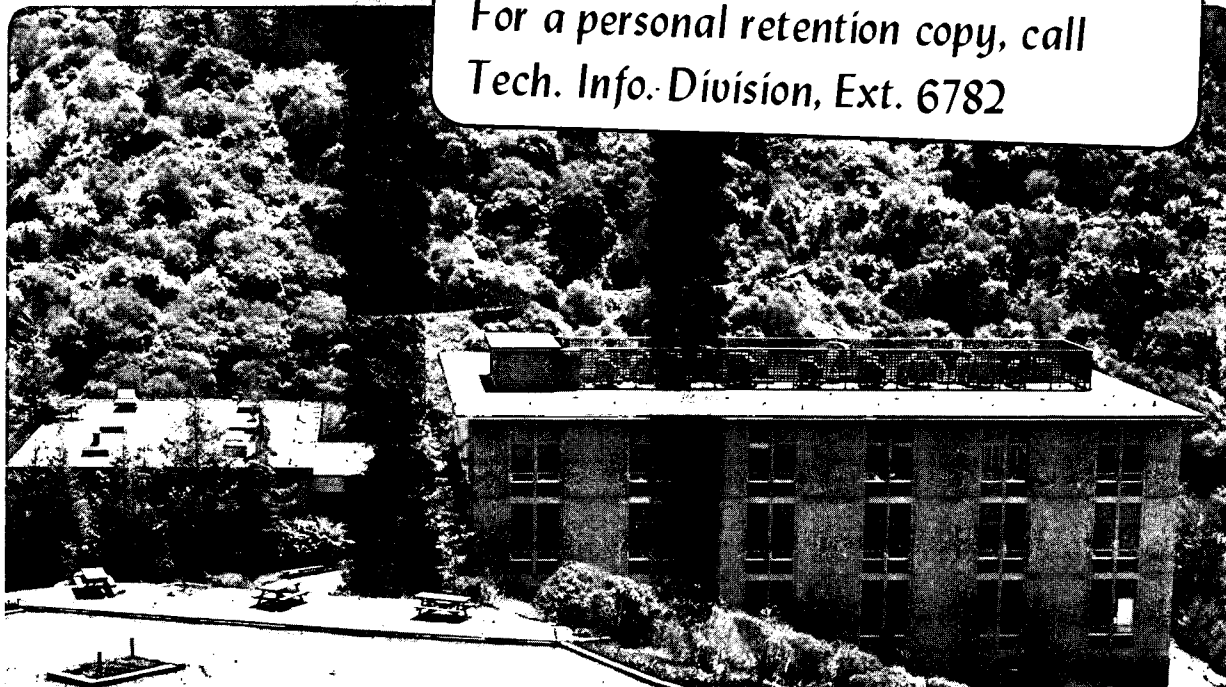Journal of Solid State Ionics

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DISCLAIMER

FAILURE MODES OF NA-BETA ALUMINA

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Degradation of sodium-beta aluminas can take two forms: Mode I and Mode II. Mode I is the well-documented electro-mechanical propagation of a preexisting microcrack in the surface of the electrolyte. The critical electrode current densities, j_{crit}, were determined below 100°C using acoustic emission detection during electrolysis. The temperature dependence and magnitudes of j indicate that the applied voltage is an important factor. Mode II, a degradation involving internal sodium formation is briefly reviewed.

1. INTRODUCTION

Sodium-beta and beta" alumina solid electrolytes may, under certain conditions, degrade when used in sodium/sulphur cells. The degradation can take two forms which we have labeled Mode I and Mode II.

Mode I degradation involves ion current focusing on a pre-existing surface crack. This mode of failure was first discussed by Armstrong et al. (1), and the model has been refined by various authors. The general aspects of this type of failure have been well documented: The ionic current focuses on a Na metal filled surface flaw during the charging cycle, generating capillary flow pressures when the cathodically plated metal is forced out. This leads to a stress intensity at the flaw tip that, depending on macroscopic current density and flaw size, may exceed the critical stress intensity factor. (2) The crack then propagates through the electrolyte causing a short circuit. Such models would predict that the critical macroscopic current density is proportional to the sodium metal viscosity, if all other parameters were constant. Below the melting point of sodium, where the plastic deformation of the sodium is dominated by diffusional processes, this would give an activation energy of about 0.46 eV (3) for the expected temperature dependence of the average critical current density for the onset of Mode I. In our experiments, we have used acoustic emission detection (4) to monitor the onset of Mode I degradation, since it was the most sensitive degradation initiation detection method. This permitted the examination of critical current density threshold dependences on electrolyte microstructure and on temperature (30-100°C).

A different type of degradation, involving internal sodium deposition was recently found in electrolytes cycled for extensive periods in Na/S cells. This degradation and its associated microcracking has been termed Mode II by us. Mode II appears to involve an alteration of the electronic properties of the solid electrolyte.

2. MODE I FAILURE INITIATION

Bar shaped samples of Na-β" alumina were subjected to increasing currents below 100°C in an argon glove box. The positive electrode was liquid Hg/Na amalgam; the negative electrode was evaporated gold. Prior to breakdown, the negative electrode was wetted with Na above 100°C by passing a small current for some time. The electrode current density at which a sudden rise in the acoustic activity of the sample was detected, was taken as the critical current density for the onset of Mode I degradation. An example is shown in Figure 1.

The data showed that a weak statistical correlation existed between the average size of the small grain fraction of the solid electrolyte. In fact, this weak statistical correlation may well be ignored. This is in contrast to the data collected on electrolytes tested similarly in Na/Na cells at 350°C; here a significant correlation existed between the average large grain size and the critical current density. These results will be reported elsewhere. The data of the tests below 100°C are shown in Figure 2, as a function of temperature in a Weibull statistics (5) plot, showing the failure probability, P_f, as a function of the critical current density, j_{crit}. The temperature dependence of the average j_{crit} is shown in Figure 3.
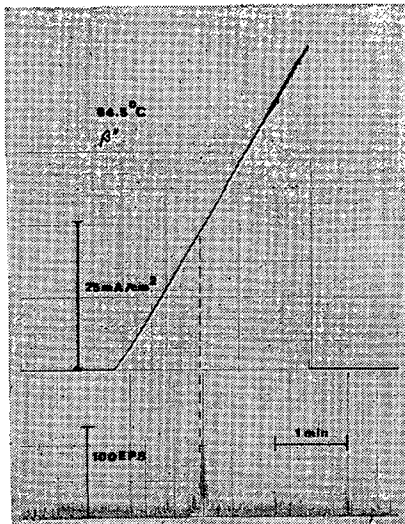
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Figure 1 : Electrode current density and acoustic emission rate in events per second (EPS) as a function of time, for a Na-β" alumina electrolyte. The onset of acoustic activity is marked.
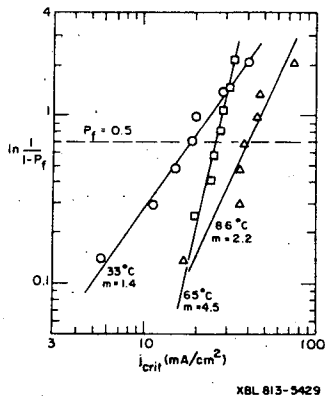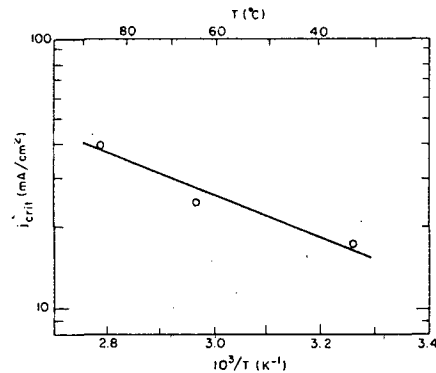

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Figure 2. Weibull statistical plot of failure probability, P_f, versus j_{crit}. The average j_{crit} occurs at $P_f = 0.5$. The Weibull statistical parameters, m, are indicated.

The activation energy for the temperature dependence of the average critical current density was found to be 0.18 eV, less than half the activation energy for sodium deformation in the temperature range studied. This indicates that factors other than mechanical stress intensity affect the critical current density threshold. The observed temperature dependence compares well with that of the ionic conductivity of beta" alumina, which is about 0.22 eV. This suggests the applied voltage is a factor that affects the critical current density for onset of Mode I degradation. The same conclusion has

been reached when the theoretical critical current densities, calculated on the basis of a detailed fracture mechanics argument, were considered. (6) These calculated critical current densities for Mode I initiation were a factor of 10^5 above the actually observed ones.

Figure 3. Temperature dependence of j_{crit} for Mode I initiation below 100°C, for sodium-beta" alumina solid electrolyte.

Local current enhancements due to unfavorable local geometries or microstructures were found to be insufficient to account for the discrepancy.

Additionally, near the melting point of sodium the average critical current density was about 40 mA/cm^2, Figure 1, while at 350°C the average critical current density was found to be about 300 mA/cm^2. If j_{crit} depended linearly on the inverse of the viscosity of the metallic sodium, as the fracture mechanics and Poiseuille pressure argument requires, the ratio between j_{crit} below to j_{crit} above the melting point should be expected to be at least 10^3. This follows from the large change in the viscosity of sodium upon freezing.

The theoretical results and the experimental data all indicate that some other process, relating to applied voltage, occurs at the crack tip. The process that is thought to occur at the crack tip is the local introduction of electrons into the solid electrolyte. This would lead to formation of sodium ahead of the crack tip, depending on the magnitude of the applied voltage, due to transport through a local transport number ratio gradient. (7) Formation of Na ahead of the crack tip would significantly lower the critical current density from the one calculated from fracture mechanics.

3. MODE II: INTERNAL SODIUM FORMATION

A second degradation mechanism, Mode II, has also been observed on electrolytes tested for long times in actual Na/S cells. (8) Darkening

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of the electrolyte as well as internal sodium deposition with associated microcracking was found to occur. The darkening was found to be due to reduction of the electrolyte by the molten sodium electrode, leading to oxygen vacancy formation charge compensated by weakly bound electrons. (9) An electronic/ionic transport number ratio gradient is thus produced in the electrolyte. Charge transfer through such an inhomogeneous electrolyte leads to internal sodium formation driven by the applied voltage, and counteracted by the counter EMF of the cell.

It could then be shown that, for a counter-EMF Δn_M^o, over the electrolyte itself, a critical charging overvoltage ΔV^{crit} over the electrolyte should not be exceeded. Under the assumptions of an invariant transport number ratio gradient and internal fracture strength of about 60 ksi, one can then find

$$\Delta V^{crit} \simeq 0.2 + 1/2 \ (0.16 + 1.6 \ \Delta n_M^o/F)^{1/2} \quad \text{Eqn.(1)}$$

To avoid Mode II onset, the applied resistance overvoltage during charging, ΔV, should be

$$\Delta V = I\rho\delta < \Delta V^{crit} \qquad\qquad \text{Equ. (2)}$$

where

F = charging current density
ρ = electrolyte specific resistivity
δ = electrolyte thickness

For a typical Na/S cell, I = 0.1 A/cm^2, ρ = 10Ω cm, ρ = 0.2 cm, and $\Delta n_M^o/F \simeq 2$ volt, we find $V^{crit} \simeq 1.1$ volt, while ΔV = 0.2 volt. Normal cell operation should thus not stimulate Mode II degradation. However, electrolyte resistance increases due to contamination, or decreases in $\Delta n_M^o/F$ due to polarization at the sulfur electrode/electrolyte interface could cause a condition where $\Delta V > \Delta V^{crit}$. Additionally, designs which require δ to increase significantly, should lead to cells which would be more susceptible to degradation, as Eqn. (2) implies.

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