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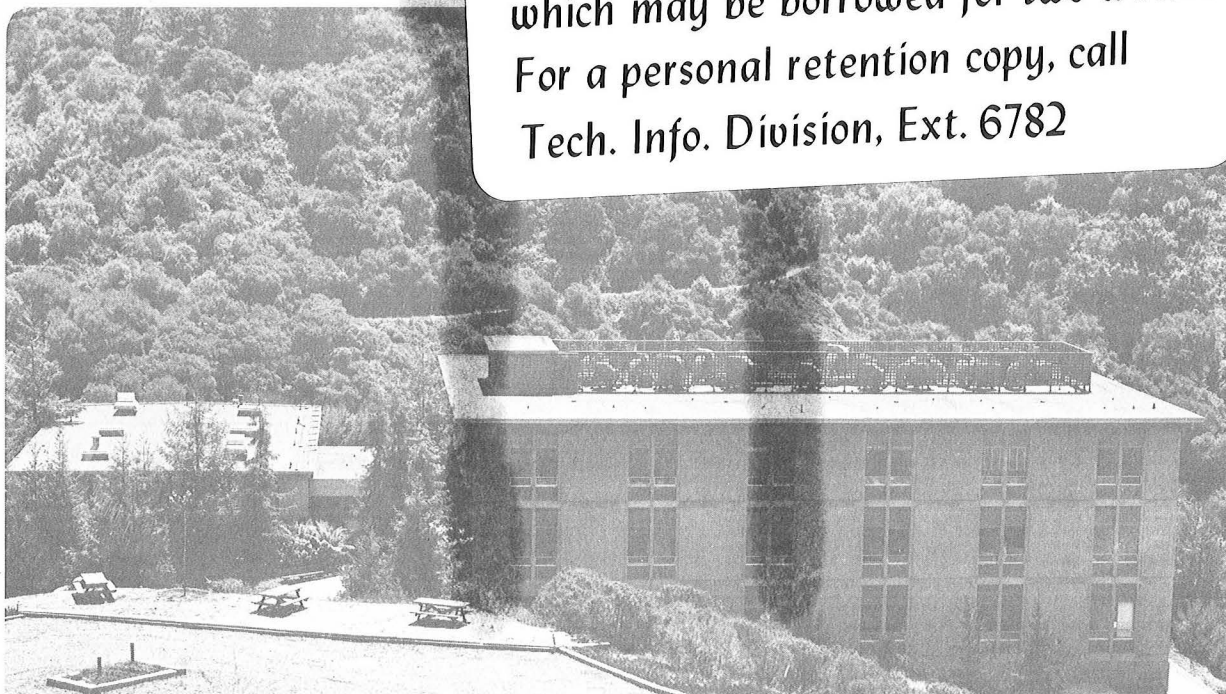
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May 1981

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PERFORMANCE OF SODIUM-BETA ALUMINA SOLID ELECTROLYTE IN Na/S CELLS

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The performance of sodium-beta alumina type solid electrolytes is limited by degradation. Two different modes of degradation are discussed. Mode I involves the well studied current focusing on a pre-existing surface flaw; Mode II involves internal sodium precipitation and possible microfracture. The second mode can be activated when a gradient in transport number ratios has been created by chemical reduction of the electrolyte by the sodium electrode. The implications of the degradation for cell operation are discussed.

I. INTRODUCTION

Beta batteries using a sodium-beta alumina solid electrolyte membrane to separate molten sodium and sodium polysulfide electrodes, are an attractive method for load leveling or for electric vehicle propulsion. While technically the battery has been proven, a key factor impeding immediate, large scale adoption of this high energy density battery has remained in question. This factor is the ultimate lifetime of the solid electrolyte in the aggressive battery environment. Significant progress towards improving the durability of the cells is continuously being made, and is reported in this conference. Although the required operating lifetime of five years appears to be almost within reach, it has not yet been achieved. It is, therefore, of importance to examine, from past experience on electrolyte failure and from recent considerations, if any electrolyte degradation mechanisms exist that cannot possibly be suppressed for a long time.

In this paper we review and expand on recent considerations on sodium-beta alumina, in-cell degradation. We find that a number of interrelated phenomena must cooperate to bring about electrolyte failure. The alteration of the electrolyte's electronic properties as a consequence of contact with molten sodium, appears to play a central role in all forms of degradation. Our considerations lead us to conclude that the electrolyte degradation can be suppressed if limits on a number of cell operating parameters are observed. These include avoiding charging over-voltages in excess of about 3 V, and operating the cell such that no polarization layers develop on the electrolyte/sulfur electrode interface.

First we discuss the consequences of the chemical action of sodium on sodium-beta aluminas, leading to electrolyte reduction and coloration. Then, the consequences of ionic conduction through a transport number ratio gradient is considered. Finally, we report on the initiation of electro-mechanical cracks (Mode I), and on the recently observed internal sodium deposition (Mode II). These considerations permit forming a framework in which the performance of solid electrolytes in Na/S cells can be understood.

II. CHEMICAL COLORATION

When sodium-beta or beta alumina electrolytes are in prolonged contact with molten sodium, a grey-brown discoloration develops from the contact interface, even without ionic charge transfer. Our experiments on single and polycrystals have indicated that the metallic sodium, in fact, reduces the solid electrolyte. The oxygen removed from the electrolyte was found to occur mainly through the spinel blocks (1), leading to

isotropic coloration of single crystals, Fig. 1a. Bleaching in air was found to be highly anisotropic, indicating that the reoxidation involved mainly oxygen transport through the conduction planes, Fig. 1b. Heating single crystals, chemically colored by prolonged immersion in molten sodium, in a very low oxygen partial pressure did not result in bleaching, Fig. 1c. These three observations demonstrated that the chemical coloration involves reduction of the solid electrolyte, leading to oxygen vacancy formation. The oxygen vacancies would be charge compensated by electrons. This can be deduced from the appearance of the broad optical absorption band, and the observation of some electronic conductivity at high temperatures (2). The absence of a narrow optical absorption band indicates that the electron-oxygen vacancy binding is weak, possibly on the order of 0.1 eV. Introduction of oxygen vacancies, which appear to behave as shallow donors, would tend to raise the Fermi level to close to the conduction band edge of the solid electrolyte. It may thus be expected that electron injection from the sodium/electrolyte interface would not be rate limiting for electron conduction through the electrolyte. The gradient in electronic conductivity that is produced for the electrolyte thus causes the existence of an electronic/ionic transport number ratio gradient. Charge transfer through such a transport number inhomogeneity could lead to internal formation of Na metal, as discussed next.

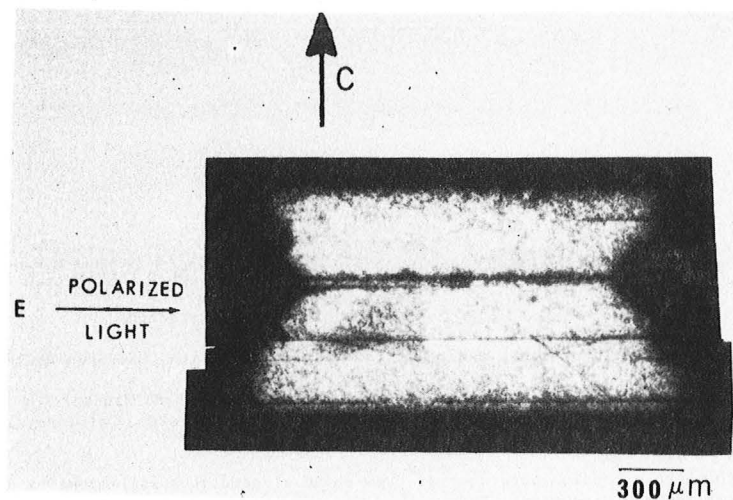
III. TRANSPORT IN AN INHOMOGENEOUS ELECTROLYTE

Charge transfer through an electrolyte containing a gradient in electronic/ionic transport number ratio was recently considered by De Jonghe (3). The chemical action of the sodium metal on the negative electrode/electrolyte interface produces a slowly evolving transport number ratio gradient. If this gradient is, in a first approximation, considered immobile during charge transfer then it can be shown that the chemical potential of the sodium in an electrolyte containing a linear gradient of the transport number ratio, can be approximated as

$$\eta_{\text{Na}} \approx \frac{x}{l} (\Delta\eta^0/FV_T) - FV_T \frac{x^2}{l^2}$$

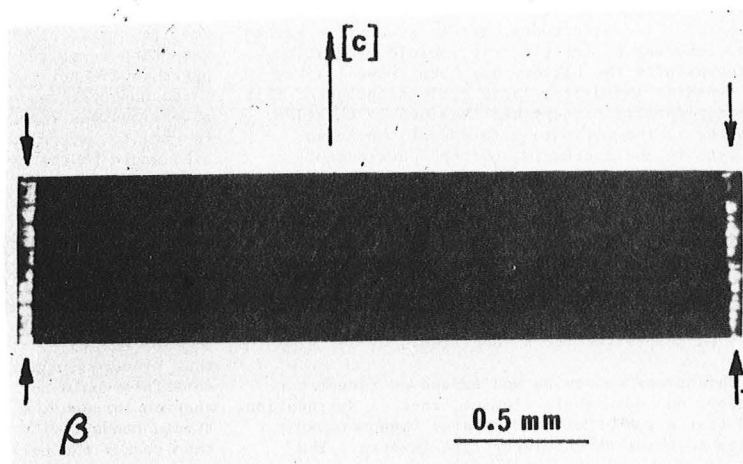
l = electrolyte thickness
 x = distance from the negative interface
 F = Faraday's constant
 V_T = Applied voltage over the electrolyte
 $\Delta\eta^0/F$ = cell counter-EMF over the electrolyte

Thus, it may be considered possible that internal electrolysis could take place, causing the electrolyte to behave similar to a distributed electrode (4). At sufficiently high V_T and with a negative electrode



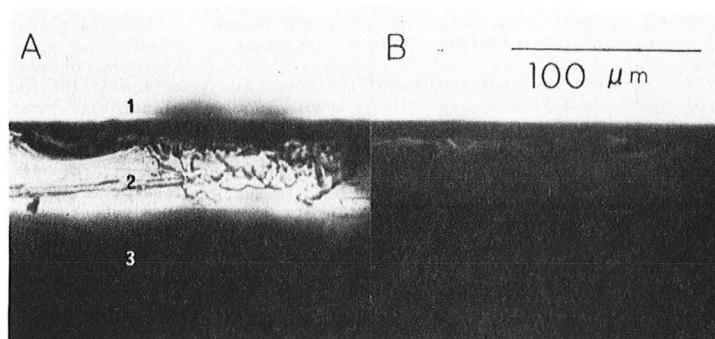
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Figure 1a. Isotropic coloration of single crystal of β alumina, immersed in molten sodium metal at 350°C . The coloration has been enhanced by silver exchange. The conduction planes are perpendicular to the paper.



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Figure 1b. Anisotropic bleaching of same single crystal upon reoxidation in air at 400°C . The bleaching proceeds along the conduction planes.



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Figure 1c. No bleaching is observed if crystal is heated in a vacuum with $P_{\text{O}_2} \approx 10^{-38}$ atm. Crystal A on left was heated in air; crystal B on right was heated in vacuum; both 24 hrs at 400°C .
1: mounting medium; 2: bleached layer; 3: colored crystal.

consisting of sodium metal, internal formation of sodium under pressure might result in electrolyte fracture.

This response of an inhomogeneous electrolyte subjected to charge transfer permits the interpretation of a variety of degradation phenomena that have been observed so far. The phenomena that it can explain include the low current density at which the Mode I degradation is initiated, and the observation of a Mode II degradation in beta battery electrolytes that had been subjected to charging voltages above 5 volts.

IV. MODE I FAILURE: ELECTRO-MECHANICAL FRACTURE

Electro-mechanical failure of solid electrolytes was first treated by Armstrong et al. (5). It described the main features of metal dendrite and associated crack propagation from the metal electrode/electrolyte interface during electrolysis. Cathodic plating of Na in a small crack and the associated current focusing on it causes crack extension by the generated Poiseuille pressure. The electrolyte then fails by propagation of such a surface crack. A number of observations have well documented this type of fracture (6-8), and a variety of treatments have refined the original argument. Disturbing in these treatments, however, is that further refinements lead to calculated microscopic current densities necessary to initiate the Mode I failure that are a factor of 10^5 too high, compared with the actual observations. In our treatment, the critical current density is found to be:

$$j_{crit} = K_{IC}^4 E^{-3} ne / (3.32\tau l) ,$$

where

- j_{crit} = the critical macroscopic current density to initiate Mode I.
- K_{IC} = mechanical stress intensity factor
- E = Young's modulus
- n = the atomic number density of sodium
- e = charge of sodium ion
- l = the crack length
- τ = the viscosity of sodium

We believe that the discrepancy lies in the assumption of the models that the mechanical stress intensity factor is identical to the electro-mechanical one during cell charging. The effects described in the previous section should bring into play a voltage as well as a current effect. From the sharp crack tips, involved in Mode I initiation, local electron injection should be possible. The injection of electrons should be facilitated by the raising of the Fermi level to close to the conduction band edge (as a consequence of electrolyte reduction, as discussed in Section II). This would cause internal sodium metal deposition by the mechanism described in Section III, just ahead of the crack tip, leading to an actual stress intensity factor at the flaw tip that is significantly higher than the mechanical one. The quantitative dependence of the actual stress intensity factor on the applied voltage or current density has not yet been established, but is under consideration. Qualitatively, these considerations are in agreement with the observation of critical current density thresholds of at most a few amps/cm² on fresh electrolytes, and the rapid decrease of j_{crit} as the temperature is lowered (applied voltage must increase to maintain the same current density). Qualitatively, it could also be predicted that if the electrolyte ionic resistance went up, e.g., as a result of contamination

by impurities, the actual stress intensity factor would be unfavorably affected since the local electric field gradient would increase.

V. MODE II DEGRADATION: INTERNAL SODIUM DEPOSITION

Our recent observations on electrolytes from beta batteries (9) indicated that internal sodium deposition with associated electrolyte microfracture could occur. An example of this type of degradation, termed Mode II by us, is shown in Fig. 2. Some Mode I fractures have also been marked in this figure. It is quite possible that a Mode II degradation evolved into a Mode I fracture through microfracture growth, or coalescence. Mode I, however, can also be induced without any demonstrable Mode II degradation.

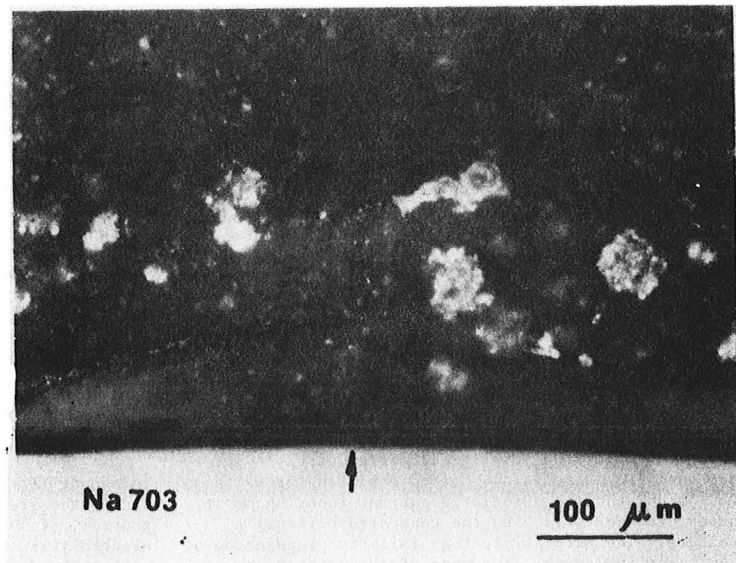
To find the critical applied voltage V_T at which this Mode II might occur requires knowledge of $\Delta\eta^0/F$ and of the electrolyte internal fracture strength. In general, if $\Delta\eta^0/F$ and the mechanical strength of the electrolytes are low, then V_T would be low. Under the reasonable assumption that $\Delta\eta^0/F = 2$ V and that the electrolyte fracture strength would be about 400 MPa (60,000 psi), a charging voltage of about 3 V would have to be exceeded before the Mode II internal degradation would occur. Although this is not much above the charging voltages used for current Na/NaS_x cells, it still permits indefinite inhibition of this mechanism if the sulfur electrode polarization can be kept low during cell operation. The electrolytes shown in Fig. 2 had in fact been subjected to charging voltages that exceeded 5 V. The Mode II degradation is not observed consistently in all electrolytes that we have examined so far. Detailed correlations of the occurrence of this Mode II degradation with cell operating conditions are currently examined.

The considerations concerning the Mode II degradation led to identifying the following factors as contributing adversely to the electrolyte performance when the cell is operated in a current controlled mode:

1. High charging current densities requiring a charging voltage, V_T , over 3 volts
2. Increased electrolyte thickness (increased V_T)
3. Increased electrolyte resistance (increased V_T)
4. Polarization layers at the sulfur electrode/electrolyte interface (decreased $\Delta\eta^0/F$)

VI. SUMMARY

The performance of sodium-beta aluminas in beta batteries is limited by two degradation modes. Based on the considerations in this paper, it should be possible to achieve a long electrolyte lifetime if certain conditions of cell construction and operation are observed. Theoretical considerations point again in the direction of avoiding cell contamination and interface polarization layers that could promote Mode I and Mode II degradation. Improved cell performance should therefore be sought in improved sulfur electrode design, improved materials corrosion resistance, and cell cycle management that avoids interface polarizations. Additional benefits might possibly be derived from altering of the ceramic electrolyte composition so that electronic conduction could be totally depressed. It is expected, however, that this might be difficult to achieve for sodium-beta or beta aluminas in contact with molten Na.



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Figure 2. Mode I (arrowed) and Mode II (large white spots) degradation is observed in this electrolyte. The electrolyte was retrieved from a sodium/sulfur cell that had operated at 325°C. The total charge transfer through the electrolyte was 703 A hr/cm² (charge + discharge).

VII. ACKNOWLEDGMENT

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VIII. REFERENCES

1. L. C. De Jonghe and A. Buechele, LBL 12440 April, 1980.
2. N. Weber, *Energy Conversion*, 14, 1 (1974).
3. L. C. De Jonghe, LBL-12070, February, 1981.
4. P. Fabry and M. Kleitz, in "Electrode Processes in Solid State Ionics," M. Kleitz and J. Dupuy, Eds., D. Reidel Publ. Co., Dordrecht, Holland, 1976, pg. 331.
5. R. D. Armstrong, T. Dickinson, and J. Turner, *Electrochim. Acta.*, 19, 187 (1974).
6. R. N. Richman, and G. J. Tennenhouse, *J. Amer. Ceram. Soc.*, 58, 63 (1975).
7. D. K. Shetty, A. V. Virkar, and R. S. Gordon in "Fracture Mechanics of Ceramics," Vol. 4, R. L. Bradt and D.P.H. Hasselman, Eds., Plenum Press, New York, 1978, pg. 651.
8. M.P.J. Brennan, *Electrochim. Acta.*, 25, 621 (1980).
9. L. C. De Jonghe, L. Feldman, and A. Buechele, *J. Mat. Sci.*, in press, March, 1981.