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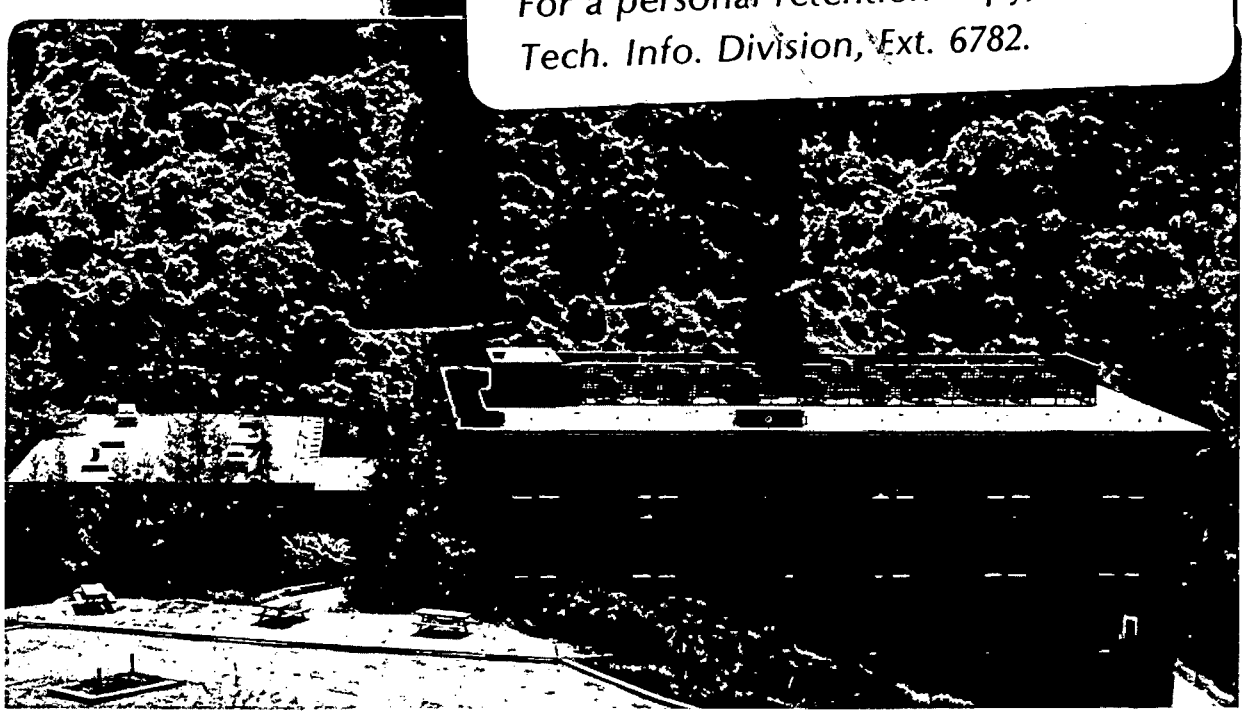

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# GRAIN BOUNDARIES AND SOLID ELECTROLYTE DEGRADATION

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Abstract

The initiation and propagation of electrochemical degradation in sodium-beta alumina type solid electrolytes has been found to involve grain boundaries. Degradation is preferentially initiated at 00.1 facets of large grains, lowering the critical current density threshold for coarse grained electrolytes. The critical current densities were determined by monitoring acoustic emissions during current flow. Direct indications of the implication of grain boundaries in degradation has been obtained from transmission and optical microscopy of degraded electrolytes.

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# I. INTRODUCTION

Sodium/sulfur batteries are high energy density storage devices that may, in the near future, be used in load leveling systems for the electric utilities or as power sources for electric vehicles. While technical feasibility has already been demonstrated, economically competitive operation has not yet been achieved. The key factor is the lifetime of the battery. The critical component in the cells is the solid electrolyte membrane, usually sodium-beta" alumina[1], which degrades to some extent during battery operation. Two modes of degradation have been reported[2]. A first type of degradation involves crack initiation at the negative electrolyte surface where Na metal is formed during the changing cycle [3]. The crack is driven by capillary streaming pressures generated when sodium metal is forced out of it after cathodic deposition. Attempts at calculating critical current densities above which incipient cracks would propagate catastrophically, have been made by several authors[4,5,6]. We have called this failure mechanism Mode I degradation. A second type of degradation, Model II, involved internal deposition of Na metal within the solid electrolyte, and is thought to be due to the effect of passing current through the ionic/electronic transport number gradient that develops as a consequence of partial chemical reduction of the electrolyte by the Na electrode[7]. The observations and theoretical considerations have been reported recently[8].

One aspect of the solid electrolytes that has not yet been assessed is the role of grain boundaries in the degradation process. In this paper we address this issue.

## II. EXPERIMENTS

Polycrystalline Na-β" alumina discs* were used in Na/Na cells, and acoustic emissions were monitored as a function of current density. Two different electrolyte microstructures with the same chemical composition were used: one electrolyte had an average grain size of 1.1μm and less than 1 vol% of grains over 10μm long (average length 14μm); the second electrolyte was more strongly bimodal with 17 vol% of grains with an average length of 1.1μm and 83 vol% of large grains, 54μm long on the average. The electrode area was 0.2 $cm^2$. The details of the experiments have been described elsewhere[9]. The acoustic emission detection proved to be sufficiently sensitive to determine the crack propagation initiation at the onset of Mode I degradation.

A series of Na exposures leading to chemical coloration[7], and of bleaching experiments were also performed on electrolytes with an average grain size of 5.4μm containing 54 vol% of grains with an average length of 15μm and 41 vol% of grains with an average size of 2.8μm. The Na exposures were carried out at 325°C; the bleachings were done in air or in a glass ampule in which oxygen had been removed by glowing a vanadium getter. The polycrystals were bleached at temperatures up to 1000°C.

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*Prepared by Cramatec, Inc., Salt Lake City, Utah 84115. Composition: 9.1 wt% $Na_2O$, 0.75 wt% $Li_2O$, balance $Al_2O_3$.

In other experiments extensive Mode I degradation was induced rapidly in Na-β alumina electrolytes through which high currents were passed in a manner described earlier[10]. Thin sections were prepared of the degraded area for examination with the transmission electron microscope.

Optical microscopy was performed in coarse grained electrolytes in which Mode I degradation had been initated.

## III. RESULTS AND DISCUSSIONS

The acoustic emission monitoring of the Na-β" alumina specimens carrying currents in Na/Na cells showed that the critical current densities for Mode I initiation were distributed according to Weibull statistics. The fine grained electrolyte exhibited a mean critical current density of 690mA $cm^{-2}$ and a Weibull modulus of 1.8; the large grained electrolyte showed a mean critical current density of 145ma $cm^{-2}$ and a Weibull modulus of 3.4. Then experiments clearly revealed that microstructure significantly affects Mode I failure initiation. Since the small grain fraction in both electrolytes was approximately the same in both electrolytes, it could be concluded that large grains adversely affected the electrolyte's behavior under current. Microstructural examination of these electrolytes indicated that the Mode I cracking had initiated in the sodium exit surface of the electrolytes, preferentially at 00.1 faceted boundaries of very large grains. Evidence of this is shown in Figure 1a. Two configurations of large grains have been marked 1 and 2 in Figure 1a, illustrating the difference in susceptability to Mode I initiation between 00.1 faceted grain

boundaries and grain boundaries involving direct spinel-spinel block bonding. The structures of the corresponding grain boundaries are shown in Figure 1b and 1c. This observation suggests that the 00.1 faceted grain boundaries are mechanically weak. Further evidence of the low bonding strength along 00.1 faceted grain boundaries can be seen in Figure 2 which shows a fracture along a partially 00.1 faceted grain boundary. The fracture occurred in-situ, as a result of stresses developed due to electron radiation induced $Na_2O$ loss and subsequent lattice collapse of the Na-β" alumina"[11-13]. In the region where the grain boundary deviated from an exact 00.1 facet, the spinel-spinel block bonding, arrowed in Figure 2, survived. The fracture path suggests that an exact 00.1 facet is mechanically weaker than the conduction (cleavage) planes, and most likely has an oxygen ion arrangement related to that of the low density conduction planes rather than that of the close packed spinel blocks. The details of grain boundary structures in beta aluminas have been discussed elsewhere[14].

A plausible geometrical argument can further be made for preferred Mode I initiation at 00.1 facets of the β on β" alumina grain boundaries. Since cleavage occurs most readily along 00.1 planes, pre-existing surface flaws would be most likely found along these planes. Such initial flaws contained within a grain can, however, not be effectively current fed due to the highly anisotropic ionic conduction[11]. An effectively current fed, sodium filled surface flaw would have to be perpendicular to the basal planes. One can however conceive of flaws at 00.1 facets that can act as effective initial

flaws. The three geometries are shown in Figure 3. Thus, the easy 00.1 cleavage, combined with the highly anisotropic ionic conductivity argues in favor of Mode I initiation at 00.1 faceted grain boundaries. Large grains are also more susceptible than small grains as a result of the usual decrease of strength with increased grain size. The same argument may be applied to Mode I crack propagation. An example of Mode I propagation along grain boundaries is shown in Figure 4, obtained from a sample that had been rapidly and extensively degraded. The dark, intergranular material in Figure 4 could be identified as sodium carbonate, the remains of the Na that was originally present before foil preparation. In rapid degradation experiments, however, the Mode I propagation path tends to be both interand transgranular. Evidence of slow crack Mode I propagation along grain boundaries has been found in electrolytes used in long-term Na/S cell tests[9].

The coloration kinetics of polycrystalline Na-β[11] aluminas as a consequence of contact with molten Na metal has been recently reported[7]. It was shown that coloration proceeded preferentially along grain boundaries. Heating colored polycrystalline electrolyte in an oxidizing environment also led to bleaching, while heating in the low oxygen partial pressure (glass ampules) did not produce significant bleaching, as is shown in Figure 5. The behavior of the polycrystals in a reducing and in an oxidizing environment is thus similar to that of the single crystals[7]. However, much higher temperatures appeared to be necesssary to produce bleaching in polycrystalline Naβ" alumina compound to single crystalline Na-β alumina. The reason for

this is, at present, not known. The grain boundary coloration reaction thus also involves a partial reduction leading to increased grain boundary electronic conduction. Since this produces ion/electron transport number gradients, one may also argue that the Mode II degradation initiation would involve grain boundaries[8]. The observation of Na deposition at some grain boundaries, a consequence of this type of degradation, supports this argument[1].

The process of the β or β" reduction by Na may also be involved in the low Mode I propagation that one can deduce from the presence of partially penetrated Na dendrites in electrolytes used in long-term Na/S testing. Indeed, when Na is electrodeposited inside a Na filled crack it is totally free of oxygen. The oxygen chemical potential in the Na metal β alumina interface in the crack is therefore established by the kinetics of the interface reduction reaction, the diffusion rate of the oxygen dissolved in the Na, and the Na flow velocity. The latter is determined by the current density[6]. One can thus construct an argument, in many ways similar to that of Richman and Tennenhouse[5], leading to slow, subcritical crack growth.

## IV. CONCLUSIONS

The experiments have indicated the electrochemical degradation of sodium-β and β" aluminas is initiated preferentially at 00.1 grain boundary facets of large grains. Such grain boundaries were found to be mechanically weak, and are geometrically favorable for effective current supply. The observations provide an explanation for the decrease in critical current density for initiation of Mode I degradation found by acoustic emission detection. Grain boundaries were found to be colored by the same mechanism as single crystals, leading to enhanced grain boundary electronic conduction. This process makes them favored sites for Mode II initiation, as well as for Mode I propagation.

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## VI. ACKNOWLEDGMENT

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FIGURE CAPTIONS

Figure 1a. Optical micrograph of silver stained[10] sodium exit surface for electrolyte subjected to unidirectional current flow of 50 $mA/cm^2$, in a Na/Na cell, at 300°C. The two configurations of Mode I initiation have been labeled.

1b. Lattice image of a grain boundary structure corresponding to 1 in Figure 1a.

1c. Lattice image of a grain boundary structure corresponding to 2 in Figure 1a.

Figure 2. Fracture at a grain boundary partially faceted along 00.1 planes. When the grain boundary deviates from an exact 00.1 facets, direct spinel-spinel block bonds (arrowed) have survived.

Figure 3. Schematic of three possible initial surface flaws. The A configuration cannot be effectively current fed; the B configuration does not involve 00.1 cleavage planes; the C configuration is both along a 00.1 plane and can be effectively fed.

Figure 4. $Na_2CO_3$ relics (dark intergranular material A) of Na metal penetrating intergranularly during Mode I propagation. Lattice image obtained by transmission electron microscopy.

Figure 5. Comparison of polycrystalline specimens bleached in air (A) and heated in oxygen free environment (B) for 24 hrs. at 1000°C. Prior coloration was produced by immersing the specimens for 15 days in Na at 350°C. Optical micrograph of silver stained cross-sections; Na exposed surface marked S; C is the mounting medium.

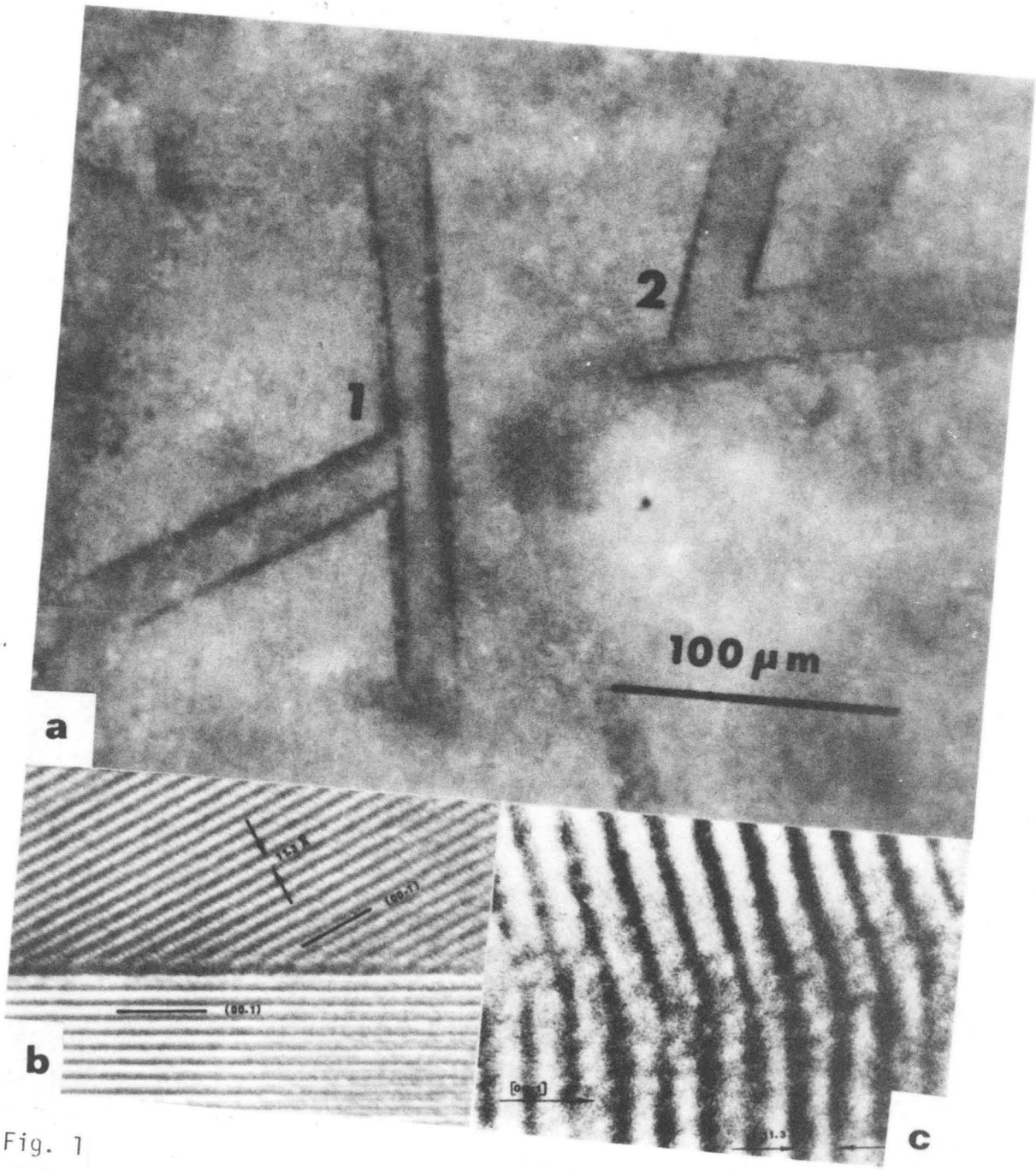


Fig. 1

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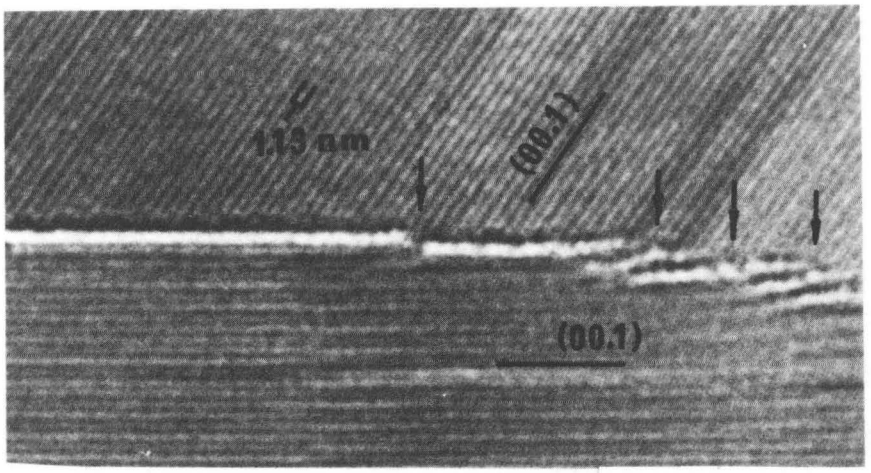


Fig. 2

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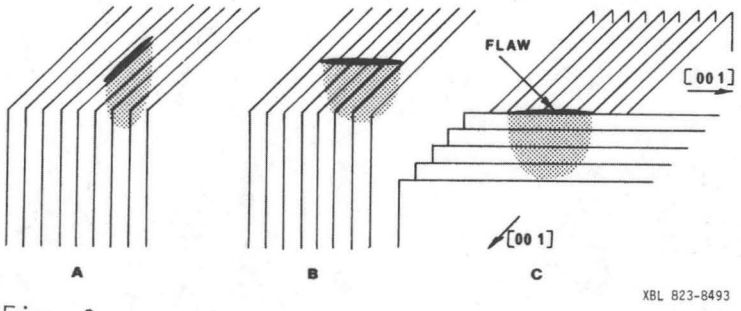


Fig. 3

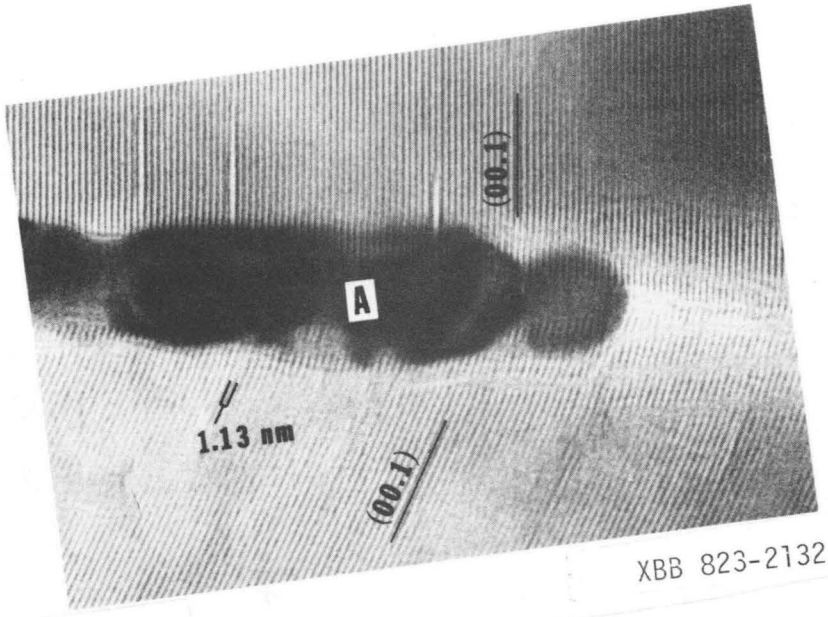


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Fig. 4

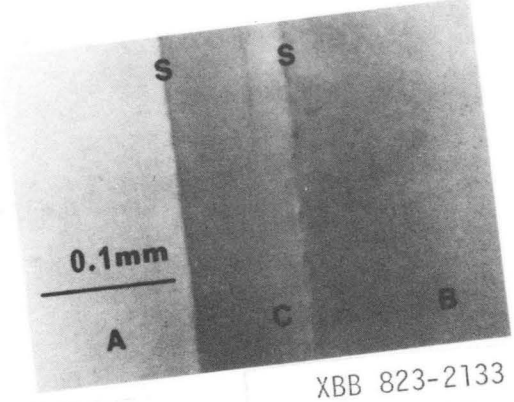


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Fig. 5

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