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INITIATION OF DEGRADATION IN POLYCRYSTALLINE SODIUM-BETA ALUMINA ELECTROLYTES

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Introduction

Sodium-beta alumina solid electrolytes degrade during use in sodium sulfur cells. The degradation can take two forms: Mode I degradation involving the rapid propagation of macroscopic cracks driven by cathodic deposition of sodium in them (1), (2); and Mode II degradation involving a slow degradation due to electron injection from the Na/ $\beta$  alumina contact (3). The initiation stage of Mode I is the most important one since cracks propagate rapidly once they are formed. In this paper, we discuss the significance of the local microstructure on the Mode I initiation. It appears that grain boundaries can be favorable sites for Mode I failure initiation.

Mode I Failure Initiation and Local Microstructure

The Mode I failure initiation presupposes the existence of small surface flaws, typically between 1 to 20 $\mu$ m long, with a crack opening less than 1000 $\text{\AA}$ . Once such flaws are filled with sodium by electrolysis, the critical stress intensity factor,  $K_{IC}$ , can be exceeded at the crack tip at sufficiently high macroscopic current densities. Current focusing on the small intruding crack is essential for the operation of the Mode I failure. The usual calculations of the critical current densities at which the Mode I failure initiates involves the solution of the Laplacian equation to describe the detailed electric field and the resulting primary current distribution on the crack phases. Approximate solutions for the secondary current distributions were recently obtained by Brennan (2). All treatments consider only solutions for isotropic solids. Beta alumina is, however, an extremely

anisotropic solid, and frequently blocking grain boundaries can be found (3). The microstructure will therefore strongly alter the current flow into cracks, especially when these are of the order of the grain size. Geometrical considerations show that cracks are most effectively fed when they are oriented perpendicular to the conduction planes, as shown in Figure 1A. However,  $\beta$ -alumina cleaves most readily parallel to the conduction planes. The next most favorable crack-feeding geometry is shown in Figure 1B, and involves a blocking grain boundary that is faceted along the conduction planes. Evidence of failure initiation, below and above the melting point of sodium, at grain boundaries such as the ones described in Figure 1, is found in Figure 2A and Figure 2B. The micrographs clearly indicate the importance of local geometry in failure initiation.

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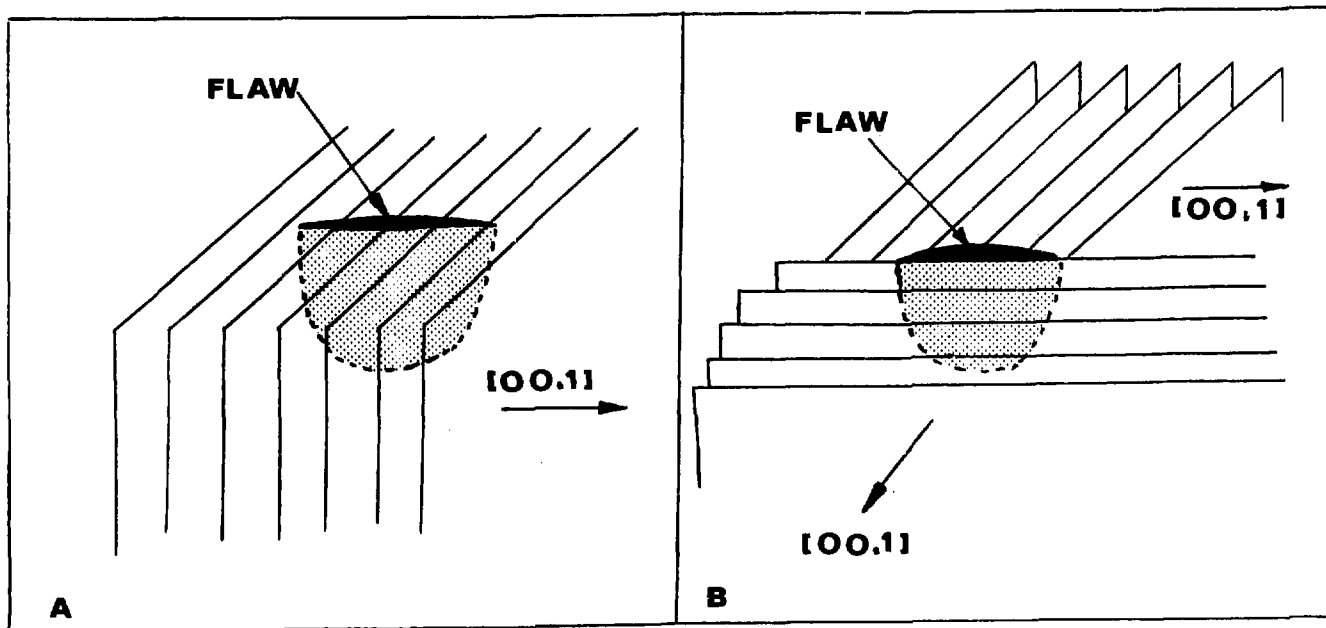


Fig. 1A Local geometry for most effective current focusing:  
 1B Local geometry for next best current focusing, involving  
 a 00.1 faceted grain boundary. XBL 805 9786

XBL 805-9786



Figure 2A

XBB 804-4130



Figure 2B

XBB 804-4117

Fig. 2A Failure initiation flaws below the melting point of sodium  
T = 65°C. The flaws start from grain boundaries. XBB 804 4130

2B Degradation initiation at 300°C, after a charge passage of 20A hrs.  
cm<sup>2</sup>. Grain boundaries are again involved. XBB 804-4117