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Publication Date

1980-05-01

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CONF-8009134--1

Lawrence Berkeley Laboratory

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Materials & Molecular Research Division

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Presented at the Third International Meeting on Solid Electrolytes, sponsored by the Japan Society for the Promotion of Science and the U.S. Department of Energy, Tokyo, Japan, September 15-19, 1980; and to be published in the Proceedings

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May 1980

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

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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/β 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 20μm long, with a crack opening less than 1000Å. 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, β-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.

Acknowledgment

This work was supported by the Electric Power Research Institute, and the Division of Materials Sciences, Office of Basic Energy Sciences, U. S. Department of Energy, under Contract W-7405-Eng-48.

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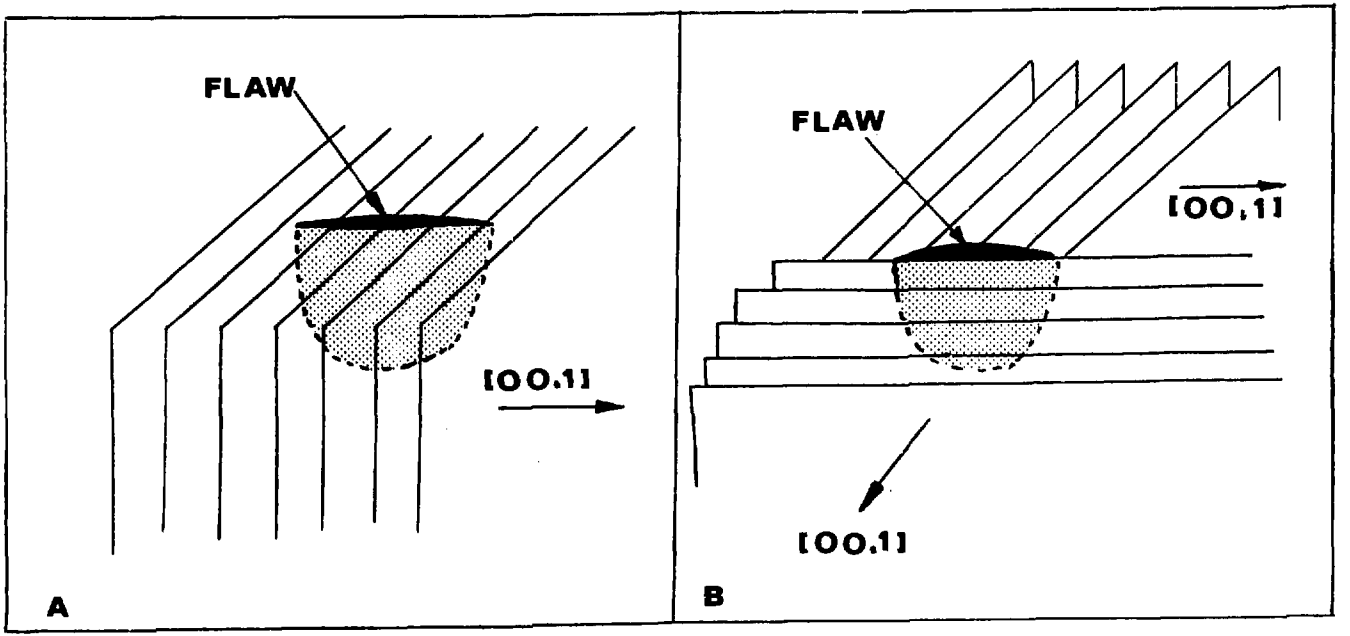

XBL 805-9786

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

Figure 2A XBB 804-4130

Figure 2B XBB 804-4117

Fig. 2A Failure initiation flaws below the melting point of sodium $T = 65^{\circ}C$. The flaws start from grain boundaries. XBB 804 4130

2B Degradation initiation at $300^{\circ}C$, after a charge passage of 20A hrs. cm^{-2}. Grain boundaries are again involved. XBB 804-4117