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TIME DEPENDENT DEGRADATION IN SODIUM-BETA" ALUMINA SOLID
ELECTROLYTES

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ABSTRACT

A slow crack propagation phase has been found for Mode I failure of sodium-beta" alumina solid electrolytes. Results from sodium/sulfur cell testing indicates the existence of a current density treshold below which slow crack growth does not occur.

Microstructural examination of used electrolytes showed in many cases the formation of a damage layer at the sodium exit side of the electrolytes. It is suggested that water contamination may be involved in this type of slow damage.

During the operation of sodium/sodium or sodium/sulfur electrochemical cells utilizing sodium beta-or beta"-alumina solid electrolytes various forms of electrochemical degradation may occur. The most significant form of degradation involves the rapid propagation of a sodium metal

* Now with InterNorth Inc., Omaha, Nebraska.

filled crack, driven by the Poiseuille pressure of sodium cathodically plated in it, leading to an electronic short circuit. (1-5) This form of degradation, Mode I, starts from a pre-existing surface flaw when a critical current density is exceeded. A possible slow mode of degradation, Mode II, was discussed by De Jonghe (6,7), and can occur when sodium is electrolysed through a solid electrolyte that contains a gradient in the transport number ratios of the electrons and the ions. Such a gradient could result from the slow reduction of the electrolyte in contact with the metallic sodium electrode and thus provide a mechanism for delayed failure. The conditions for the initiation of this type of delayed failure appear to require overvoltages that are not normally encountered in the operation of cells, unless impurities or significant electrode polarization are present. However, observations on electrolytes used by battery developers under conditions where the Mode II failure was unlikely to be active showed evidence of other forms of slow degradation. Additionally, failure initiation testing in which the rate of the current increase was varied indicated slow crack growth associated with Mode I failure. We report on these observations here.

MATERIALS

Sodium beta"-alumina disks were prepared by Ceramatec, Inc., Salt Lake City, Utah, by a method described by Miller et al. (8), except that the disks were formed by cold die pressing before sintering. The microstructures and the composition were similar to those described

earlier (9). Certified ACS sodium from Fisher Scientific Company, Santa Clara, California was used in Na/Na cells made with these electrolytes.

Used electrolytes were obtained from a number of manufacturers. Although these electrolytes do not represent the current state-of-the-art, they have nevertheless provided insights into various forms of degradation.

Electrolytes from the Compagnie Generale d' Electricite (CGE), Marcoussis, France, had been tested unidirectionally for 1000 hrs at 100 mA/cm^2 (100 Ah/cm^2), in sodium/sodium cells. These tubes had been operated with the inside as the sodium entrance surface.

Electrolytes from the early sodium/sulfur cells of the British Railway Research and Development Division, Derby, U.K., had a composition of 8.9 wt% Na_2O , 0.7 wt% Li_2O , balance Al_2O_3 , and were more than 90 vol% beta", with the remainder beta-alumina. These cells had been subjected to an average current density of 50 mA/cm^2 , with a current density up to 100 mA/cm^2 on some discharge cycles. The cells were of the inverted design, with the sodium polysulfide electrode inside the electrolyte tubes.

Some used electrolytes were also provided from batteries tested by the Ford Motor Company, Aeronutronics Division, Newport beach, California. These electrolytes had been manufactured by Ceramatec, Inc., and had

the same composition and sintering cycle as the disc-shaped samples described above.

EXPERIMENTAL

The electrolytes were examined by optical and scanning electron microscopy. Specimens for the optical microscope were sectioned with a diamond saw, ground with silicon caribe abrasive, and polished to a one micron diamond finish. They were subsequently stained with a silver nitrate solution at 80°C for about 20 min (10), to reveal the degraded regions as dark features against a light background when viewed with polarized light in the optical microscope. In some specimens a mechanically weak surface layer was present, requiring a more careful grinding and polishing with one micron diamond paste on a plate covered with tin. With this procedure good edge retention could be achieved.

To detect the onset of Mode I degradation acoustic emission testing was used. The method has been described in detail earlier, (9) in the present work disk-shaped rather than tube-shaped electrolytes were used. Sealing was accomplished with SBW sealing glass, Schott America, New York. The cells were preheated to 350°C for 30 minutes to promote the wetting of the electrolytes, and were tested at 300°C. A molybdenum electrode was inserted in the cell, making direct contact with the electrolyte, and Na was plated on it at a very low current density to form the working electrode. Filling the inside of the cell

in this way minimized impurity contamination. The plating process was monitored with the acoustic emission system to eliminate specimens in which Mode I degradation had been initiated during cell filling. The electrolytes were tested by passing an increasing ionic current and recording the moment at which acoustic activity commenced or became continuous. To assess the possible presence of slow crack growth a number of electrolytes were tested with two different rates of current increase. The current ramp was generated with a programmer and galvanostat such that the current through the cell started at zero and increased linearly with time. The acoustic activity during this test was recorded.

RESULTS AND DISCUSSION

Acoustic emission studies of critical current densities. Initiation of Mode I degradation depends on the statistical distributions of pre-existing surface flaws and current densities. The Mode I initiation is an extreme value statistical phenomenon and Weibull statistics should be expected to be suitable for their description. Since the electrodes were of finite shape, a geometric correction needed to be made to the modified by the finite values of the exchange current densities. It can be shown that the survival probability for the equivalent uniform electrode current density, P_S (uniform), equal to the average macroscopic value is related to the measured survival probability, P_S , by

$$P_S(\text{uniform}) = P_S^{1/C}$$

where C is a function of the electrode current distribution and the Weibull modulus, n . The value of C was found to be 1.33. Both P_S and P_S (uniform) have been shown in Figs. 1-3. The statistical method for the determination of the secondary current distribution, and the determination of C have been described in detail before by Buechele et al. (9).

Na/Na cells were subjected to currents increasing at a rate of $1\text{mA}/\text{cm}^2\text{sec}$ and of $10\text{mA}/\text{cm}^2\text{sec}$. Figures 1, 2, and 3 show that the critical current density for initial and for continuous acoustic emission and for a drop in cell resistance all increased when the rate of increase of the current density was higher. The dashed lines give P_S , while the solid lines give P_S (uniform). Each datum point in these graphs represents the result of a separate test. The initial acoustic emissions were somewhat difficult to distinguish at the $10\text{mA}/\text{sec}$ ramping rate and only one reliable datum point could be obtained. The results are summarized in Table I. The effect was greater for the initial than for the continuous emission and was least for the drop in cell resistance. The results indicate that the time dependence for the initiation of Mode I degradation is greater than for the propagation of the Mode I cracks, showing that the crack velocity is high once the critical current density has been exceeded. The increase of the average current density for Mode I failure initiation indicates that time dependent, electrochemically assisted crack growth can be active at low current densities. Since mechanical stress assisted slow crack growth does not appear to be active, (3, 11) it is reasonable to assume

that during slow growth the crack tip velocity would be determined by the current density at the crack tip only. This current, I_{tip} , is proportional to the crack length over the crack opening displacement, c/r , and to the macroscopic current density, I . (6).

Assuming that the crack opening displacement does not vary strongly with crack length, allows some further speculations on the slow crack growth process. This assumption will overestimate I_{tip} . The crack tip velocity, \dot{c} , can then be expressed as

$$\dot{c} = A I^m c^m \quad \text{Eqn. 1}$$

where a is a proportionality constant. At some point the crack will then reach a critical size, c_c , and propagate catastrophically, driven by Poiseuille pressure. In the present experiments the current is increasing at a constant rate, I_0 , so that

$$I = \dot{I}_0 t \quad \text{Eqn. 2}$$

If it is assumed that the critical crack size, c_c , is large compared to the initial crack size, c_i , when the stress intensity (12) at the crack tip, caused by Poiseuille pressure, has reached the critical value, then Eqn. 1 may be integrated to give

$$t_f = \left[\frac{c_i^{1-m}}{(m-1)A \dot{I}_0^m} \right]^{1/(m+1)} \quad \text{Eqn. 3}$$

The value of the exponent m then follows from a comparison of observed times to catastrophic crack propagation, t_f , at two different values of I_0 , from

$$t_{f1} / t_{f2} = \left[\dot{I}_{02}^m / \dot{I}_{01}^m \right]^{m/(m+1)} \quad \text{Eqn. 4}$$

From the data listed in Table 1, m is then found to be:

$$m \approx 2.25$$

An approximate value of A in Eqn. 1 can be determined if some assumption is made about the size of the initial crack, c_i . It has been demonstrated previously that failure initiates preferentially at the grainboundaries of large grains (13). The large grains are typically on the order of 50 to 100 micron in this electrolyte. Assuming c_i to be about 50 microns leads to

$$A \approx 1.3 \times 10^{-11} \text{ } \mu\text{m/sec (mA/sec) } \mu\text{m)}^m \quad \text{Eqn. 5}$$

It is interesting to use these values of m and A to estimate a time to catastrophic crack propagation for actual cell condition, where the electrolyte operates at a constant current density of about 100 mA/cm² during its charging cycle. At constant current density integration of Eqn. 1 gives a time to catastrophic crack propagation equal to:

$$t_f = c_i^{(1-m)} / A (m-1) I^m \quad \text{Eqn. 6}$$

Using the approximate values of A and m, Eqn. 6 and a minimum c_i of 10 micron would lead to a predicted upper bound on the failure time of about 1×10^5 sec, or a little over one day.

This value, although only approximate, is clearly much too low, since electrolytes have been known to operate at 100 mA/cm² for more than a year. Within the limits of the assumptions made here, the experiments then seem to indicate that some current treshold would exist below which slow crack growth does not occur. In some ways this is a result

that tends to support a crack growth process along the lines discussed earlier by Richmann and Tennenhouse (14).

Failure analysis of cycled electrolytes. - A sectioned, polished and stained electrolyte from a CGE sodium/sodium cell, Fig. 4, shows the three features near the electrolyte surface in contact with the molten sodium found commonly in used electrolytes: a wide darkened layer, marked A; a narrower, intensely darkened layer, marked B; and a crack with a somewhat more darkened band around it (arrowed).

The band of discoloration, marked A in Fig. 4 has been shown to result from the partial reduction of the electrolyte by contact with molten sodium. (15) No Mode I cracking of the electrolyte has been found to be directly associated with this chemical darkening under normal cell operating conditions, although it may be implicated in the Mode II degradation. (6,7)

The crack shown in Fig. 4 appears to have been arrested in the electrolyte, but serial sectioning of a number of cracked electrolytes invariably indicated that such cracks had breached across. This would indicate that the Mode I cracks, once they reach the critical size, propagate rapidly. From the thickness of the darkened band around the crack, Fig. 4, it is possible to deduce its approximate time of formation. The darkening surrounding the crack is of a similar nature as the chemical coloration band marked A in Fig. 4. This chemical coloration has been determined to proceed with a parabolic time dependence, (6,16) and comparison of the layer thickness of A and of

the discoloration band around the crack then gives the crack formation time as about 12 hours before the end of this 1000 hr test.

A feature common to most if not all used electrolytes is the narrower, but more intensely darkened layer at the sodium exit side, marked B in Fig. 4. This strongly darkened layer does not develop when the electrolyte is in static contact with sodium, but only appears as a result of electrolysis. A scanning electron microscope examination of this surface layer revealed that it had been weakened by microcracking, leading to numerous pull-outs during the polishing. To study the degraded layer, a one-way sodium/sodium cell was constructed and operated in the glove box at an electrode current density of 100 mA/cm², at 300 C, for a total of 152 hours. The electrolyte revealed again a strongly discolored thin layer at the sodium exit side, but not at the entrance side, as shown in Fig. 5, showing that this phenomenon was not due to one particular electrolyte composition.

A similar degraded layer was also found in the early British Rail electrolytes, as shown in Fig. 6. In the case shown, calcium contamination, as determined by semi-quantitative x-ray dispersive analysis in the scanning electron microscope, coincided with the damage. It is interesting to note here that the presence of impurities such as calcium, lowering the ionic conductivity, may promote the Mode II degradation (7).

Not all examined electrolytes show the extra-darkened degradation layer after use. As an example, Fig. 7, an electrolyte cycled by Ford for

592 Ahr/cm₂ in a sodium/sulfur cell at the usual charge and discharge current densities appeared completely free of any forms of degradation. This result demonstrates that the slow degradation processes observed in association with the formation of the "extra-dark" discoloration layers observed in many other electrolytes are not an intrinsic form of degradation but may be due to some, as yet unidentified, impurity. In this respect, water contamination may be a possible suspect since it was reported by British Rail that an electrolyte removed from the cell and exposed to 100% relative humidity showed substantially more surface layer damage after continued cycling than a cell comparably tested but not intentionally exposed to water vapor. This possible involvement of water contamination in slow degradation is currently under investigation.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Fig. 1 Weibull plot of the first acoustic activity as a function of the average current density at 1 mA/sec and at 10 mA/sec. The solid lines show P_S (uniform) while the dashed lines show P_S .

Fig. 2. Weibull plot of the onset of sustained acoustic activity as a function of average current density at 1 mA/sec and at 10 mA/sec. The solid lines are for P_S (uniform); the dashed lines are for P_S .

Fig. 3. Weibull plot of the first all resistance drop as a function of average current density at 1 mA/sec and at 10 mA/sec. The solid lines show P_S (uniform) while the dashed lines show P_S .

Fig. 4. Polished and stained cross-section of electrolyte to 100 Ah/cm² in a Na/Na cell by CGE. The various features are discussed in the text. Ex marks the sodium exit surface.

Fig. 5. Sodium exit (B) and sodium entrance side (A) of electrolyte tested unidirectionally in a Na/Na cell at 300 C for 15.2 Ah/cm². The direction of Na⁺ transport is indicated. Optical micrograph of polished and stained cross-section.

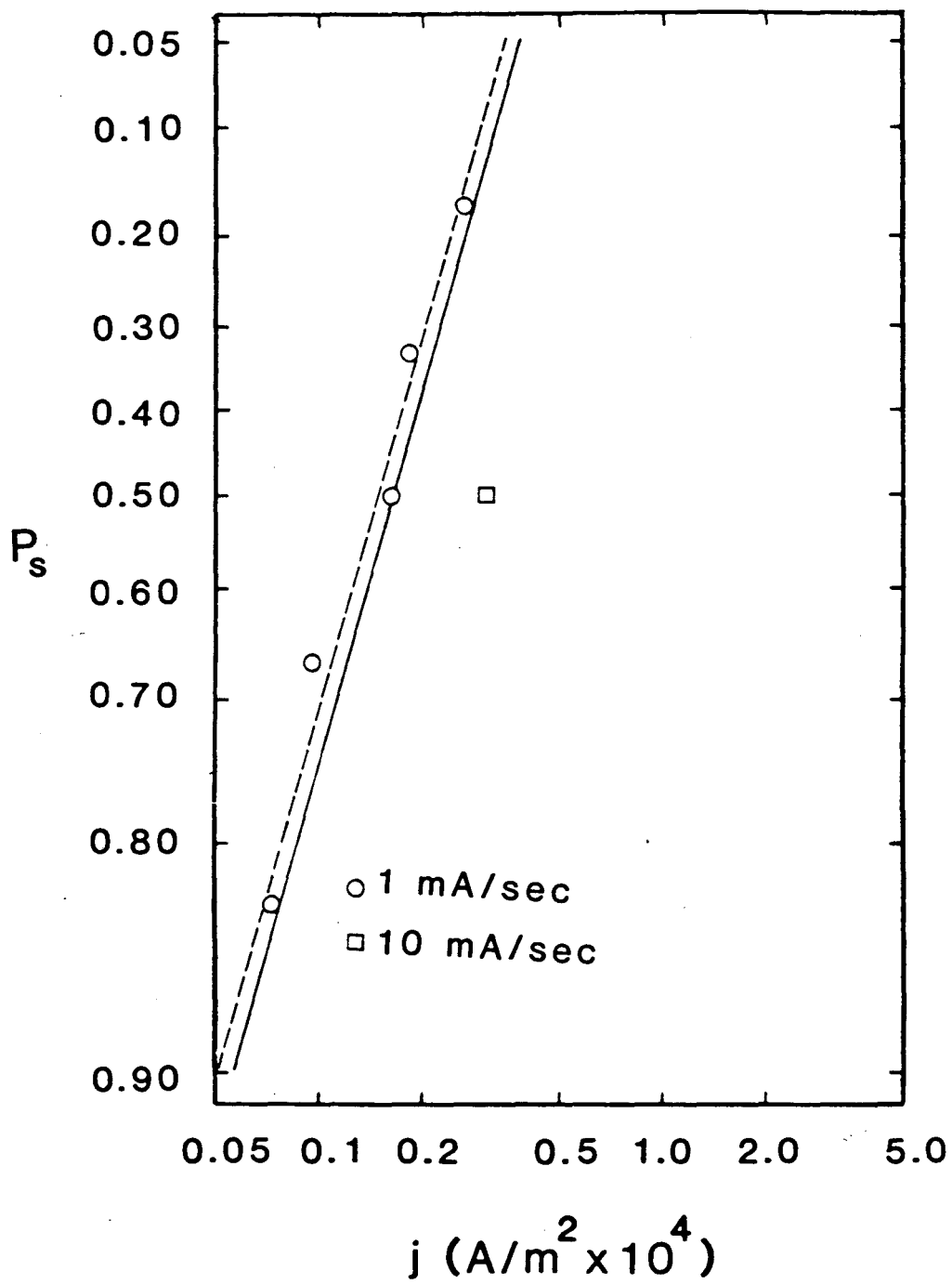
Fig. 6. Degraded surface layer and corresponding Ca content of an electrolyte tested by British Rail. The Na/electrolyte interface is marked by the arrow. The material to the left is mounting material. Scanning electron micrograph of polished cross-section.

Fig. 7. The layer of "extra" - darkening shown as B in Fig. 4 is absent in this electrolyte tested in a Na/S cell at Ford Aeronutronics Division. Na marks the sodium side; S marks the sulfur side in this optical micrograph of a polished and stained cross-section.

TABLE I

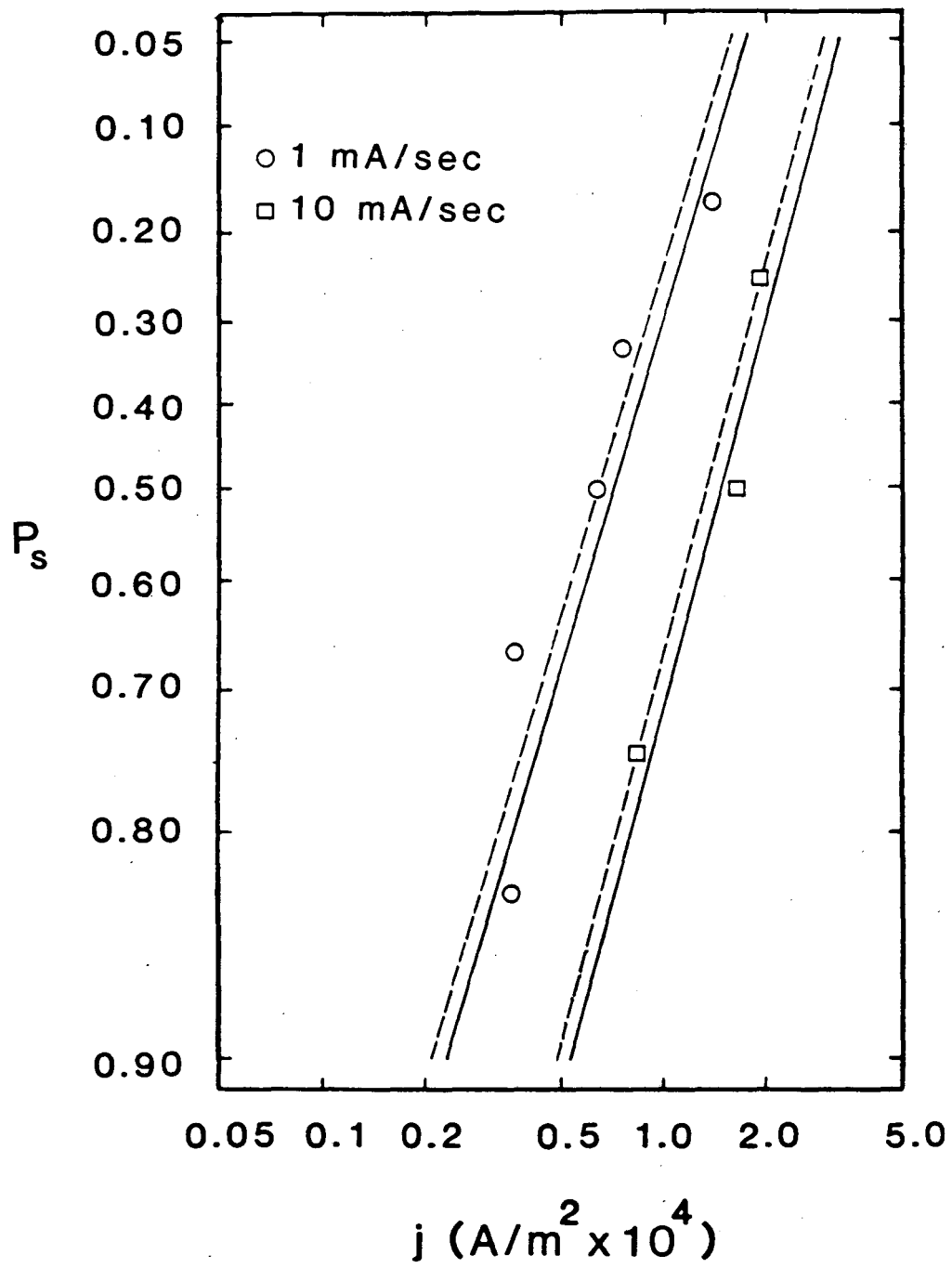
ACOUSTIC EMISSION TESTING RESULTS

I_o	onset	I_c (mA/cm ²) countinous	voltage drop
1 mA/sec	153	600	1300
10 mA/sec	(310)	1205	1580



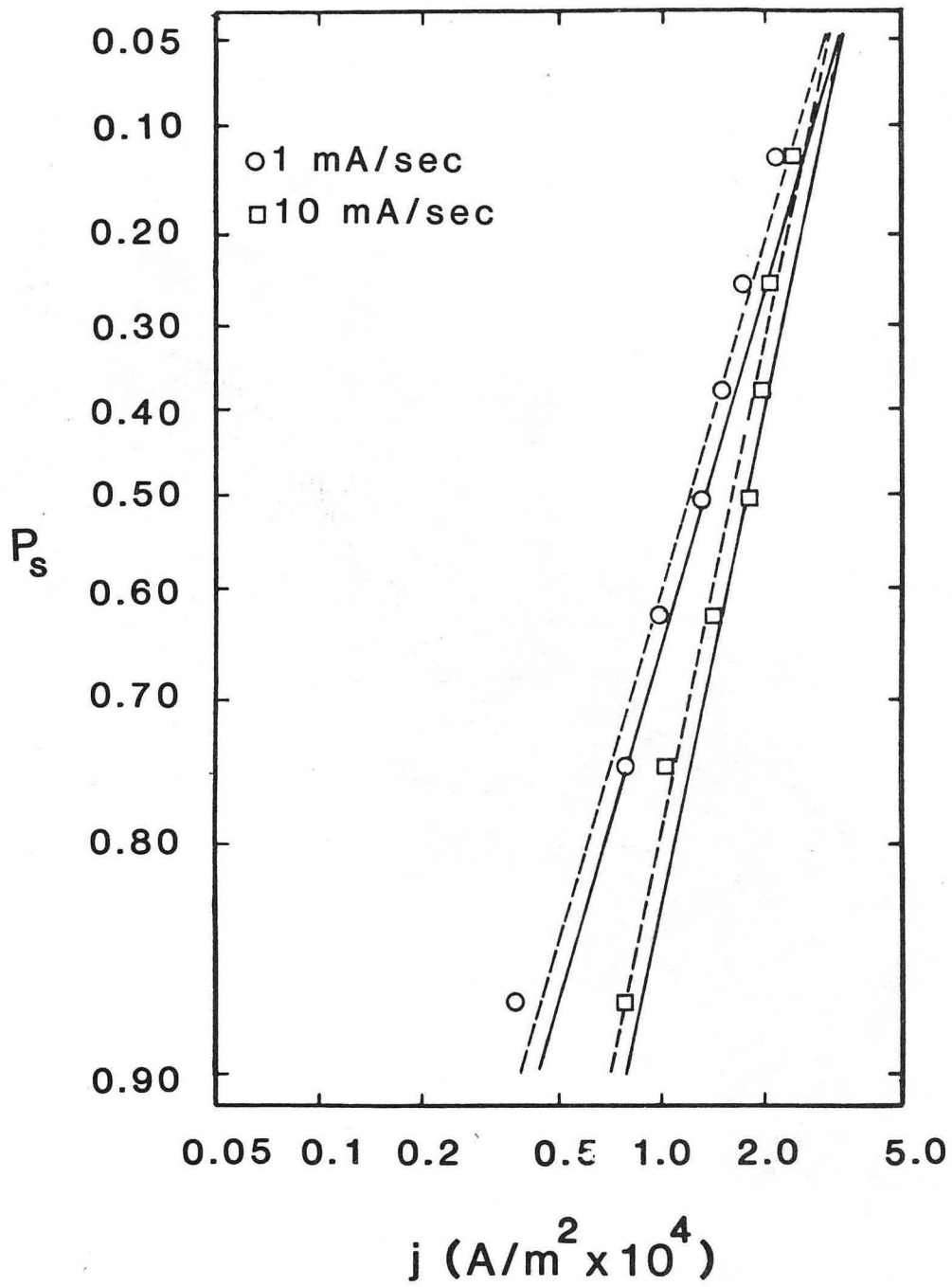
XBL 8411-4849

Fig. 1



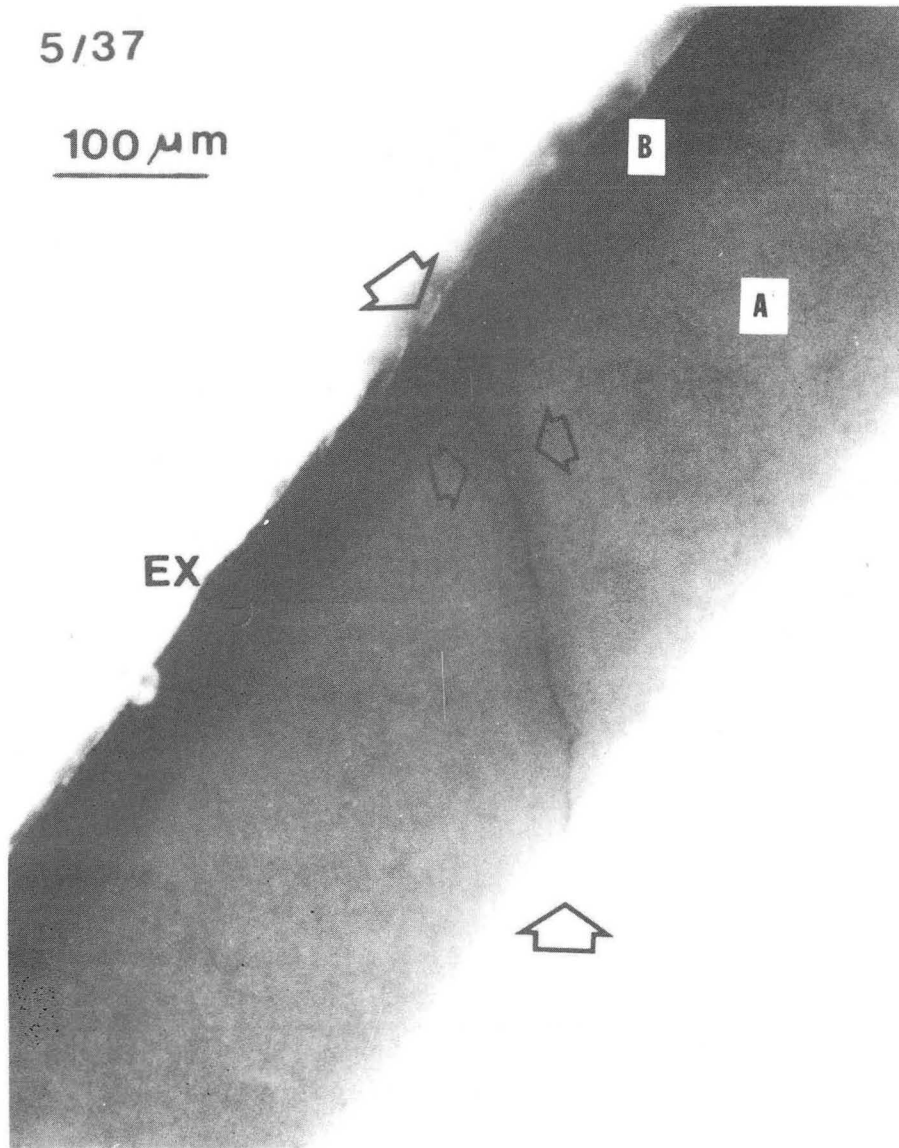
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Fig. 2



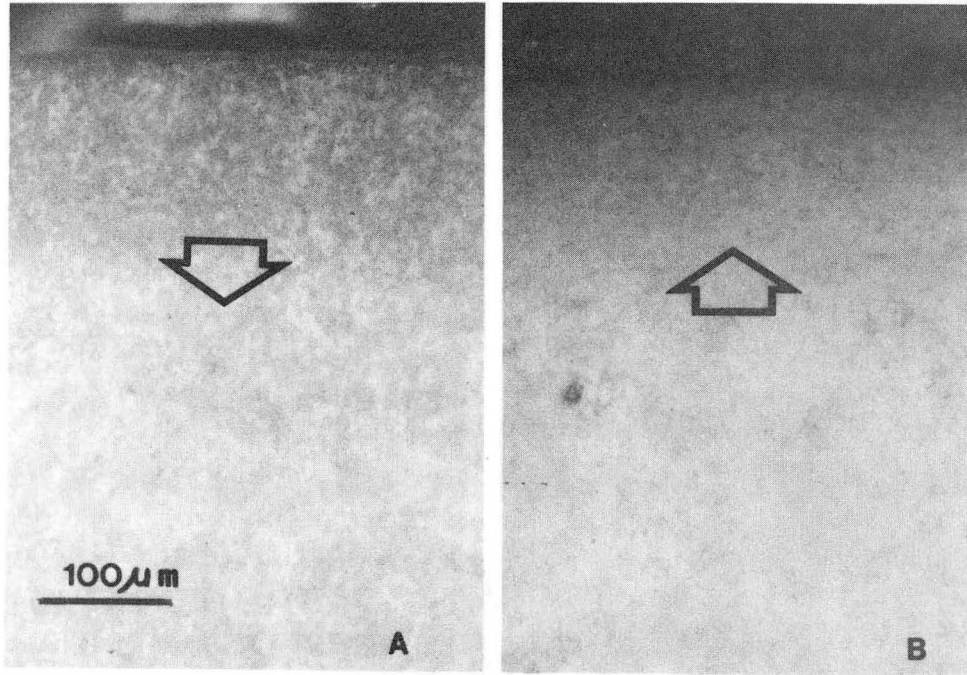
XBL 8411-4847

Fig. 3



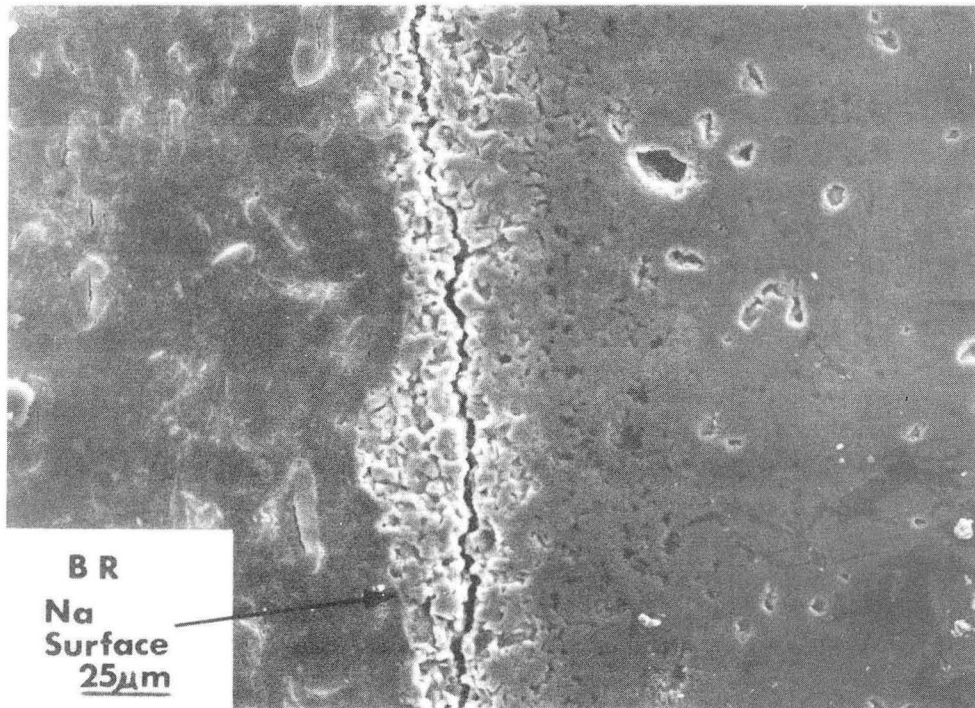
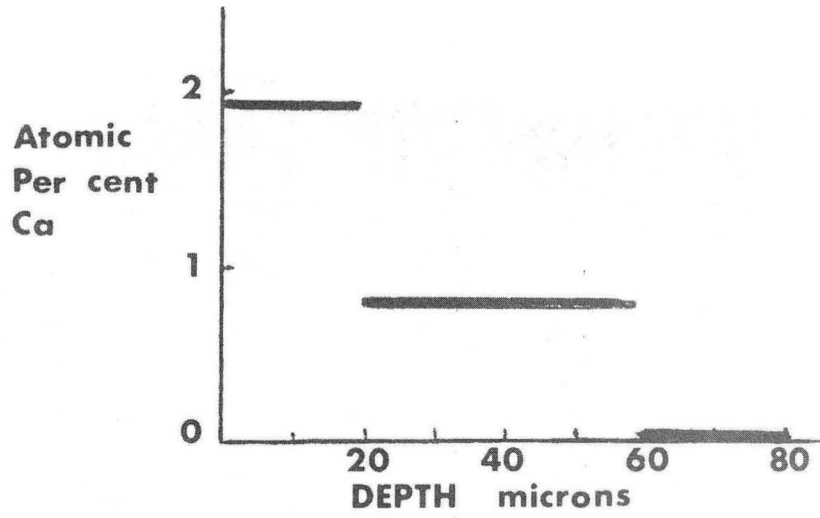
XBB 826-5037A

Fig. 4



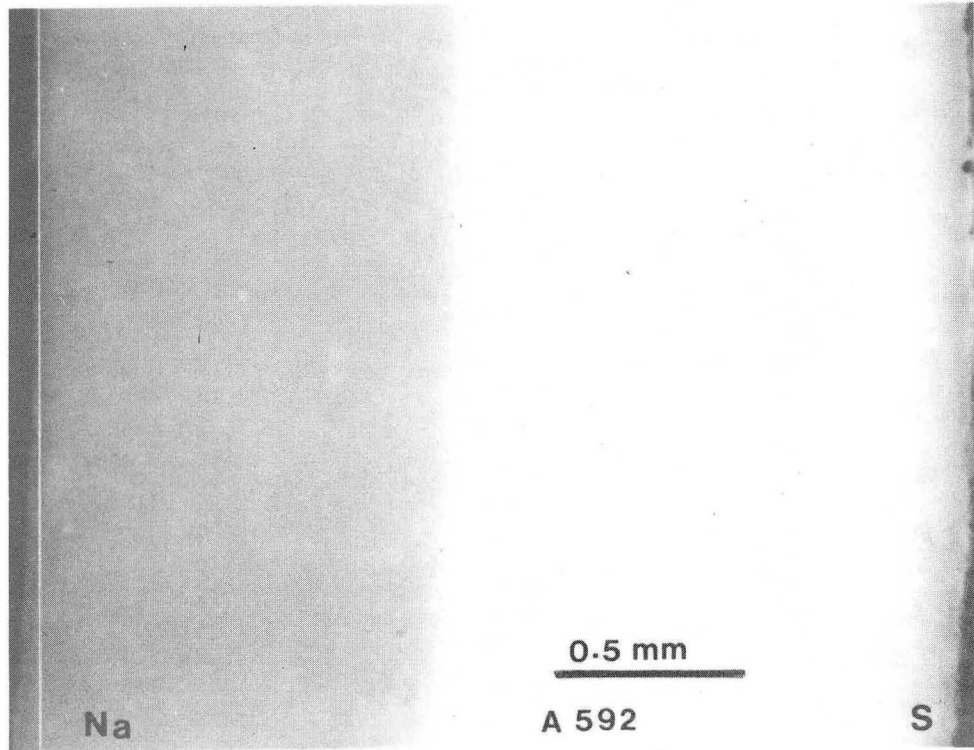
XBB 829-10690

Fig. 5



XBB 830-8823

Fig. 6



XBB 820-10682

Fig. 7

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