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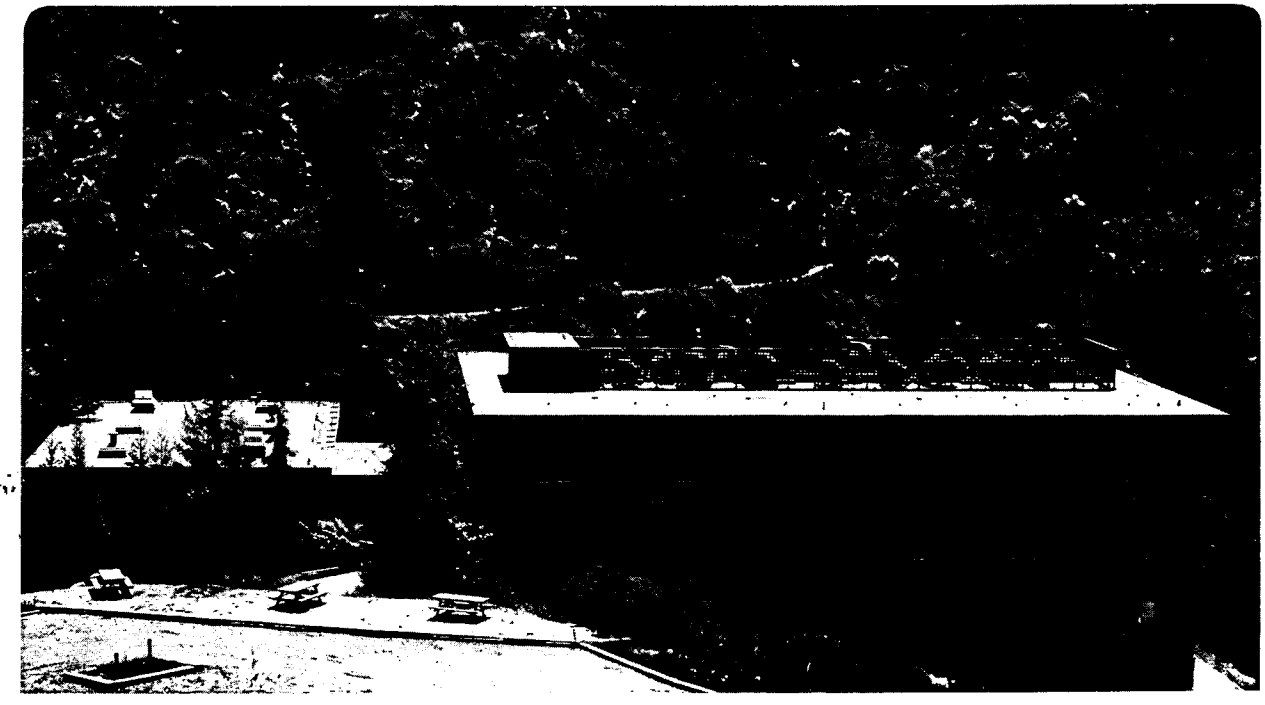

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SOLID ELECTROLYTE FOR HIGH ENERGY DENSITY BATTERIES

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INTRODUCTION

High energy density and high power density electrical storage batteries can be used to increase the efficiency of large scale electrical energy generating systems or to power electrical vehicles. The technical and economical requirements for such batteries are quite severe. They have to be of low cost, and their energy density should exceed 100 watt hours/kilogram, while there peak power output should be above 100 watt/kilogram, with a service life that exceeds five years. To date, it is only the sodium sulfur solid electrolyte system that is recognized as being able to possibly fulfill all the requirements. Considerable development of the battery has taken place since its invention.[1] Performance of existing sodium/sulfur cells is now at a level where commercialization can be envisaged, on a limited scale, within five years. Successful development of a dependable battery with the desired characteristic will indeed create a very substantial technology. A most serious problem facing the commercialization of the system is that its reliability is not yet sufficiently high. While individual cells have achieved impressive cycle lives of 2,000 or more over a period of more than one year, the distribution of failure times is still a source of concern. When failure times are plotted in a Weibull representation, then the Weibull shape factors are generally around 2 to 3, where 8 to 10 would be desirable.

A schematic of the battery construction is shown in Fig. 1. The ceramic sodium beta"-alumina solid electrolyte separates the molten sodium metal negative electrode and the molten sodium polysulfide postive electrode. To enhance current transport the positive electrode

incorporates graphite felt. This is necessary because the molten polysulfide has a very low electronic conductivity. The cell operates at about 350°C, to permit the electrolytes to be molten and to enhance the current transport through the ceramic. At the same time, this temperature widens the composition domain in which the positive electrode can operate. The polysulfides are the most corrosive compound in the battery, and the cell container has therefore to be protected from electrochemical corrosion. At present, this is done by plating the positive electrode container, consisting of mild steel, with chromiun based alloys, such as E-brite, but present results seem to indicate that this alloy may still not give sufficient protection for the required 5 to 10 years of cell operation. A search for better corrosion protection coatings is underway at the Argonne National Laboratory. The electrolyte tube header consist of alumina, sealed to the tube with a glass. Seal failures account for a significant fraction of present cell failures, and therefore additional development of sealing techniques appears needed. The outer container is sealed to the alpha alumina disk with a thermal compression bond, and appears to be performing satisfactorily. Cell failure may originate from a variety of primary causes, such as improper cell assembly, seal failure, or container corrosion. The eventual cell failure often involves the catastrophic fracture of the ceramic electrolyte, causing an internal short circuit of the cell. Therefore, the performance of the ceramic solid electrolyte in the sodium/sulfur cells continues to be of importance. Investigations of the failure mechanisms of the ceramic electrolyte under conditions of current exchange have shown that these failures may be controlled if certain precautions are taken with regard to electrolyte microstructure, and cell operating conditions and construction. In this paper the mechanisms for cell failure and the possible means of avoiding activation of these failure processes are reviewed. The paper focuses on the studies performed at the Lawrence Berkeley Laboratory.

Our examination of electrolytes that have been used by cell developers in long term sodium/sulfur cell testing, and of electrolytes that were tested in sodium/sodium cells in our laboratory, have indicated that a number of progressive changes can occur in the solid electrolyte. Some of these progressive changes can be related to the eventual electrolyte failures. Figure 2 shows the variety of degradation types that have been observed. Figure 2a is a cross section of a used electrolyte showing a darkened layer and a sodium filled crack. Figure 2b shows the internal formation of sodium metal in an electrolyte that had been used in a sodium/sulfur cell. Figure 2c shows a shallow degradation layer on the sulfur side of this cross section of an electrolyte used in a sodium/sulfur cell.

The difficulty in the understanding and the control of the various degradation processes has been that the effects may be interactive, and that various, difficult to trace impurities, may have a significant effect on the severity of the degradation. The various forms of degradation can be summarized in four categories:

1. Chemical coloration: The darkening of the electrolyte after prolonged contact with molten sodium.

2. Mode I degradation: The penetration of sodium filled cracks through the solid electrolytes.

3. Mode II degradation: The internal formation of metallic sodium.

4. Sulfur side attack

These four main degradation phenomena are now discussed in more detail.

Chemical coloration: After extended contact with molten sodium, the beta"-alumina solid electrolytes have been observed to develop a layer of discoloration that proceeds from the surface with a rate that is parabolic.[2] The discoloration involves the removal of oxygen from the beta-alumina by the molten sodium, with the charge compensation occuring by the introduction of electrons. This discoloration can be strongly enhanced if the sodium ions in the exposed samples are exchanged with silver ions. The discoloration can be completely removed if the exposed samples are reheated in an oxidizing atmosphere. The kinetics of this bleaching process have shown some anomalies at 250°C, indicating that the transport of the oxygen in the electrolyte involves two different types of oxygen interstitials, depending on temperature.[3] The experiments clearly showed that oxygen may be removed from the solid electrolyte in sufficiently reducing atmospheres. Additional discoloration may also involve the solvation of metallic sodium into the electrolyte.[4] This latter process appears to become increasingly important at temperatures above 500°C.

The intrinsic electronic conductivity of the sodium beta"-aluminas at 300 - 400°C, is quite low, around 10^{-15} ohm cm. The discoloration process raises the intrinsic electronic conductivity of the sodium-beta alumina by about 2 orders of magnitude.[5] Since the intrinsic electronic conductivity at 300 or 400°C is on the order of 10^{-15} ohm cm, this increased electronic conductivity resulting from the partial reduction of the beta alumina has no measureable effect on the Faradaic efficiency of the cell.

When electrolysis is occuring, it may be possible for the oxygen chemical potential at the sodium/solid electrolyte interface to be changed significantly from its static value. Sodium metal, used as the electrode in the battery usually contains a non-negliable amount of oxygen, in spite of efforts to remove it. Electrolysis will then cause a pile-up of oxygen at the sodium entrance side of the solid electrolyte, and a depletion at the sodium exit side. Since oxygen ions are transported in the opposite direction of the sodium ions in the beta-alumina, the sodium that is being during electrolysis at the sodium exist side is free of oxygen, and the oxygen concentration can therefore drop without limit. This can produce a very strongly reducing condition at the interface, so that destructive reduction of the electrolyte becomes a possibility after prolonged, one-way cell testing.[6] An example of an electolyte tested in such a manner is

shown in Figure 3, after a one-way test in a sodium/sodium cell, for 200 Ah/cm^2 at 100 mA/cm^2. A degraded surface layer is observed at the sodium exit side, where oxygen depletion occured, but not at the sodium entrance side where oxygen pile-up took place. The rate at which the oxygen interface concentration drops depends on the current density and on the diffusion rate of the oxygen dissolved in the molten sodium electrode. At the usual current densities at which the electrolytes operate in the cell, 100 mA/cm^2, this interface concentration drops rather slowly, approximately a factor of 3 after 24 hours, so that this type of uniform degradation should not occur in sodium/sulfur cells which are cycled once or twice a day.

Mode I degradation: Rapid and Slow Crack Growth. A frequently observed failure of the solid electrolytes consist of the penetration of a sodium filled dendrite through the electrolyte from the negative sodium electrode, during charging of the cell. This type of degradation was first examined by Armstrong et. al.,[7] and was subsequently studied in more detail.[8-11] The mechanism of failure is one in which a pre-existing surface crack, usually of the size of the largest grain, is extended under the influence of an internal sodium pressure. The internal pressure is generated when sodium is created in the crack as a consequence of electrolysis. The flow of the cathodically formed sodium out of the crack generates pressure, Poiseuille pressure, that is a consequence of capillary flow. The current density at which the crack will propagate, the critical current density, can be calculated on the basis of certain geometrical assumptions regarding the crack shape. The critical current density for failure initiation is then found to be proportional to the critical stress intensity factor, a quantity that expresses the mechanical fracture toughness of the electrolyte, raised to the fourth power. Thus, the mechanical integrity is an important quality of the solid electrolyte. Efforts have therefore been made to increase the fracture toughness of the solid electrolyte by incorporation of a partially stabilized zirconia dispersion.[12-15] The zirconia particles act in two ways: the stress of the approaching crack transforms the particles from the tetragonal to the monoclinic phase, thus creating a compressive stress field around the crack tip that opposes crack extension; and, the particles limit grain growth during the fabrication of the ceramic, thus limiting the size of the flaw origins.[22] Measurements of the critical current density of dispersion-toughened beta-alumina solid electrolytes have indeed shown an improvement in the resistance of the electrolytes to failure initiation. It is clear that the use of dispersion strengthened solid electrolytes could represent a significant step forward in the cell reliability. One factor that remains to be determined, however, is whether or not the zirconia affects the electrolytic stability of the electrolyte in any way.

Measurements of the crack-initiation current density by acoustic emission detection have shown that a slow crack propagation mode may also occur.[16] The mechanism for the slow crack propagation would involve the destructive reduction at the crack tip by the oxygen-free sodium that is formed during cell charging. Inside the cracks the current density is much higher than at the electrolyte surface, since the ionic current

concentrates on the sodium filled crack tip, so that now the oxygen concentration can be very strongly depressed. It can also be shown that a steady state oxygen concentration becomes established at the crack tip in a matter of minutes. This oxygen concentration depends not only on the current density and the temperature but also on the crack length. If it is assumed that destructive reduction of sodium beta-aluminas could occur at oxygen chemical potentials between those for the reduction of titanium dioxide and aluminun oxide, then a threshold can be calculated for destructive reduction in terms of current densities and crack lengths. It was found that at a current density of about 100 mA/cm^2, cracks should be no larger than 50 microns if destructive reduction is to be avoided. Table I shows the results of the calculation, giving the oxygen concentration at the crack tip, relative to the oxygen bulk concentration of the sodium electrode, during cell charging, as a function of current density and crack length. These findings then indicate that control of microstructure of the electrolyte is not only important for the suppresion of rapid crack growth, but for that of slow crack growth as well.

Internal sodium deposition: As was shown in Figure 2c, internal sodium deposition may also occur in the solid electrolyte.[17] This, however, is not frequently observed and, generally, electrolytes appear to be free of this type of degradation. The internal deposition of sodium becomes a possibility when currents are passed through electrolytes that contain a gradient in the ionic/electronic transport number ratio.[18] If, for example, a current is passed through an electrolyte that is partly electronically conducting on one side and an electronic insulator on the other, then the electronic current is controlled by raising the chemical potential of the electron/ion recombination product: metallic sodium in this case. This leads to the internal precipitation of the sodium. The possibility of internal precipitation of metallic sodium, leading to the formation of sub-surface cracks can be increased if the ionic resistivity is increased at the same time as the electronic conductivity in the electronically conducting layer. Such a situation results when the sodium electrode contains impurities, such as calcium, that get incorporated in the electrolyte during cell operation.[19] A gradient in the electronic resistance can be brought about by the reduction reaction described earlier, that results from the contact of the electrolyte with the molten sodium electrode.

The process described above indicates one way in which impurities may adversely affect the cell operation. Other impurities, such as oxygen and water in trace amounts, are also difficult to avoid and have been shown to contribute significantly to the electrolyte/sodium electrode interface impedance. The presence of these impurities leads to the formation of a highly resistant sodium oxide or sodium hydroxide film at the interface between the sodium metal electrode and the solid electrolyte. The incorporation of a titanium or vanadium getter has been shown to control this problem completely, and to lead to a considerable improvement in wetting of the electrolytes by the sodium, even at temperatures below 200 C.[20] Similar scavengers for potential impurities in the positive

electrodes, such as transition metals, have, at present, not been developed, but could also play a very beneficial effect on the cell operation.

Sulfur side attack: When sodium beta"-alumina ceramic solid electrolytes are used for extended periods in actual sodium/sodium polysulfide cells, it is frequently found that a shallow layer of degradation develops slowly in the electrolyte from the sulfur electrode. At present, no electrolyte failures can be attributed to this type of degradation, since the damage appears not to be very extensive. However, no cells have yet been tested for the required five to ten year period, and thus, this type of degradation should not be ignored. Static immersion at 400°C, for periods up to ten weeks, in our laboratory have indicated that the solid electrolytes developed a reaction layer at the surface.[21] The reaction seem to be most pronounced for the sulfur-rich sodium polysulfide compositions, when free sulfur is also present. An example of the formed corrosion layer after the static immersion is shown in Figure 4. The corrosion products have been tentatively identified as sodium and aluminum sulfates. Such a reaction of sodium polysulfides with sodium beta-aluminas appears to be thermodynamicaly favorable, based on estimates from the available free energies of formation. The continued corrosion at the sulfur side of the electrolyte, under dynamic electrolytic conditions, is then probably due to the removal of the partially protective reaction layer by the process of current exchange. Removal of this layer will then permit the continued attack, preferentially along grain boundaries. While the sulfur-side attack is not yet fully understood, the results so far indicate that this type of degradation may be minimized by proper design of the sulfur electrode, avoiding the localization of currents such that the electrolyte surfaces would only be exposed for a miminum amount of time to the most corrosive electrode composition.

Summary

High energy density batteries, consisting of sodium/sodium polysulfide electrochemical couples, separated by the ion conducting ceramic electrolyte sodium beta"-alumina, are now at the stage where commercialization is realistic. The detailed study of the various degradation processes occuring in the solid electrolytes, have been shown to be avoidable by microstructural control of the electrolytes, limiting the grain size to below 50 micron everywhere, by controlling the contamination levels of the system during operation, and by proper cell design that avoids current heterogeneity.

Continued development of the electrolytes by improving and optimizing the fracture toughness together with the ionic conductivity, and by developing positive electrode container coatings that have a lower corrosion rate, should prove to be beneficial to the lifetime of the cells.

Acknowledgements

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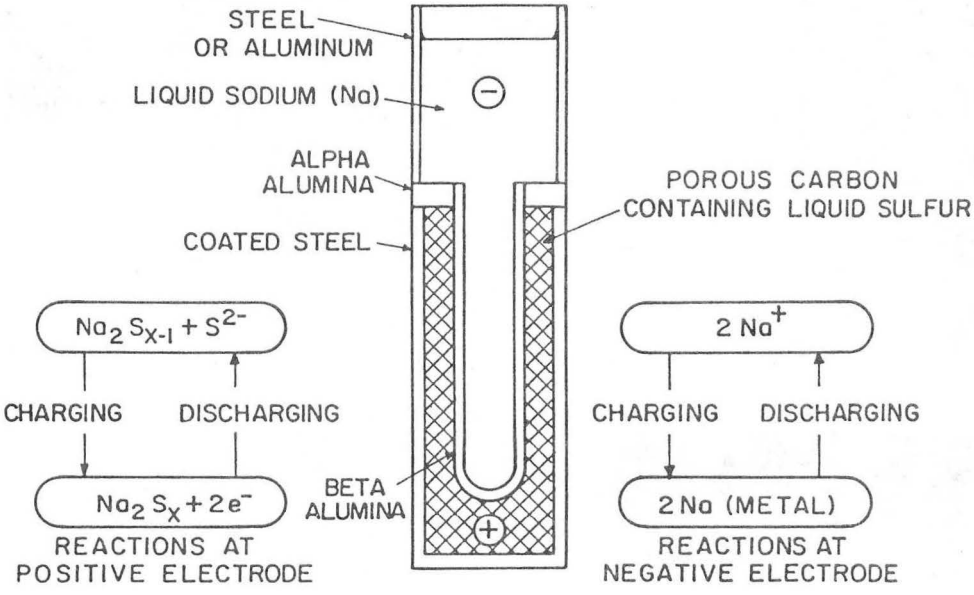
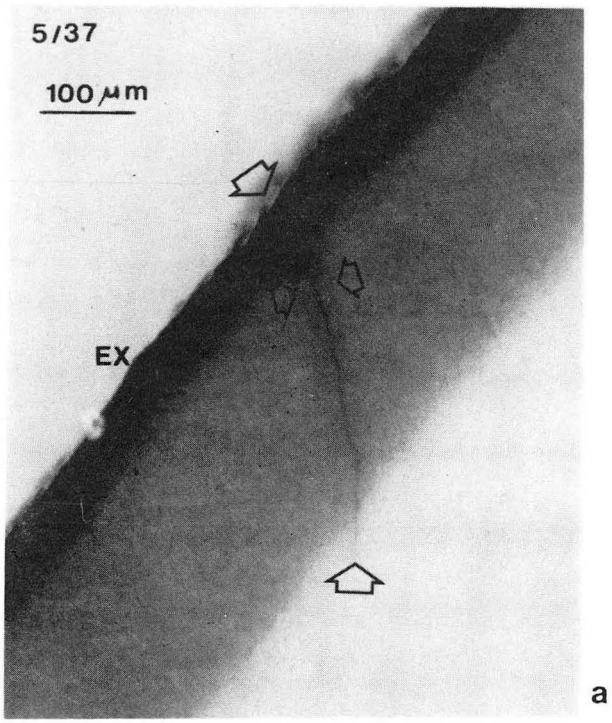
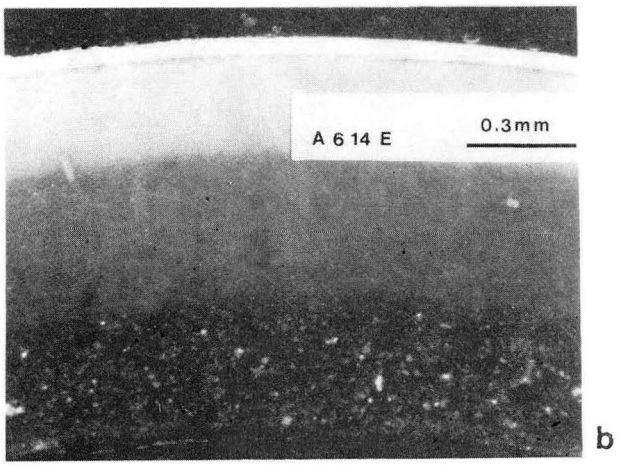


Figure 1. Schematic of a Na/sulfur cell.





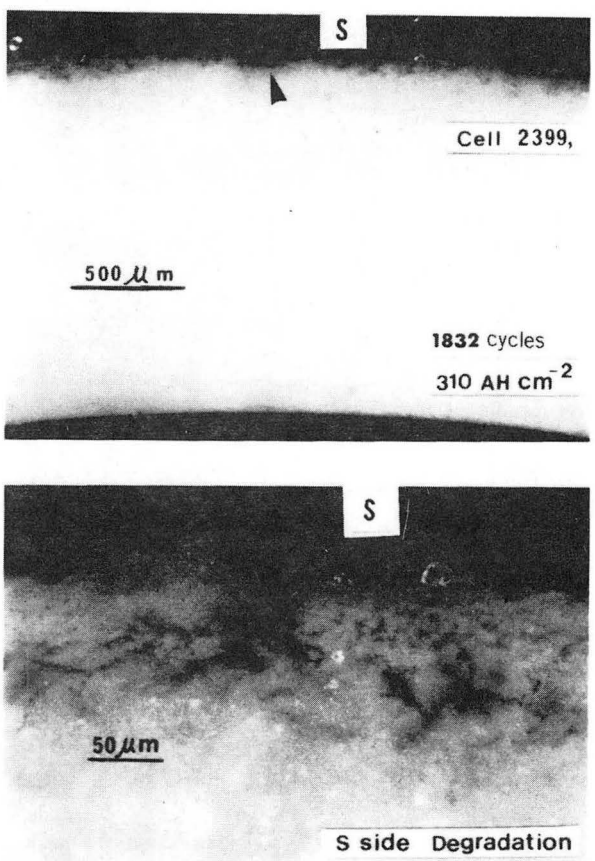


Figure 2. Types of degradation found in used solid electrolytes
a) Chemical coloration layer and sodium-filled cracks are shown in this cross section (electrolyte tested by CGE, France) XBB 826-5037
b) Internal sodium deposition is shown in this cross section (electrolyte tested by GE, USA) XBB 830-8690
c) This cross section shows sulfur-side degradation of the electrolyte. (Electrolyte tested by Brown Boveri, Germany). XBB 840-8296

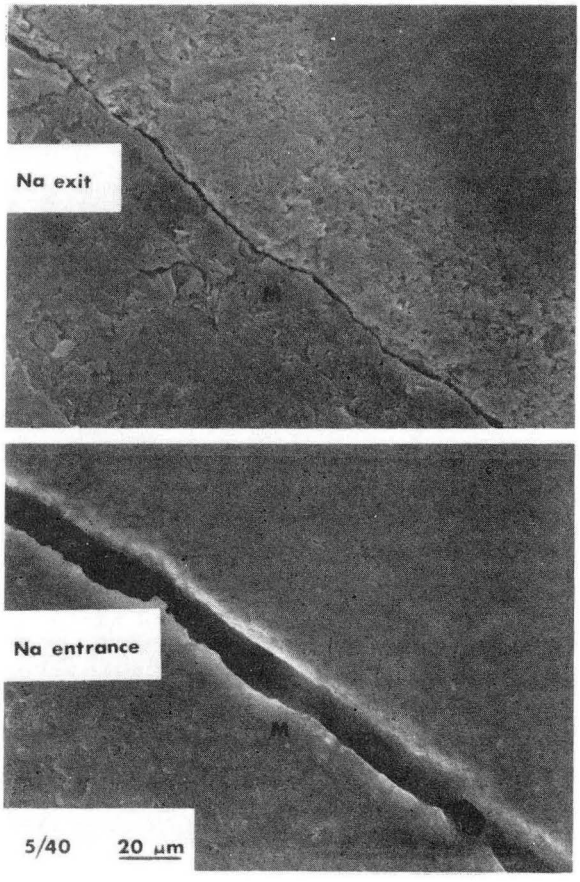


Figure 3. Degradation layer in the sodium-exit side of electrolytes tested for 200 Ah/cm^2 in a one-way sodium/sodium cell. (electrolyte tested by CGE, France); M is the mounting material. No degradation occurs at the sodium-entrance side. XBB 842-1416

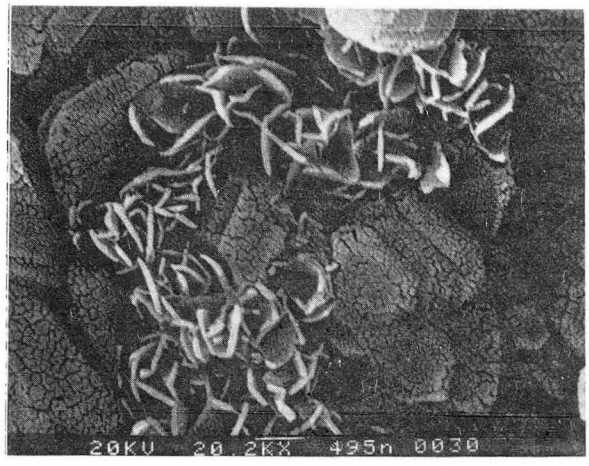


Figure 4. Corrosive layer of sodium and aluminum sulfates forward after static immersion at 400°C in Na_2S_5. XBB 851-8607

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