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Slow degradation and electron conduction in sodium/beta-aluminas

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Slow degradation was observed in sodium/beta-alumina electrolytes subjected to long term in cycling Na/S cells. The degradation propagated as a layer from the sodium side. It involves the internal deposition of sodium metal during current passage. This Mode II degradation was distinct from chemical colouration and from the Mode I failure (Poiseuille pressure due to cathodic deposition driving isolated cracks). Degradation was also observed on the sulfur side of the electrolyte and was associated with the graphite felt "imprinting effect." It is thought that the Mode II degradation resulted from electron conduction into the solid electrolyte from the beta-alumina/sodium metal interface during the charging cycle.

1. Introduction

Sodium/beta-aluminas used as solid electrolytes in sodium–sulfur batteries degrade during cell cycling. The type of degradation reported frequently to date was first discussed Armstrong *et al.* [1], and has been examined in more detail by a number of authors [2–10]. This degradation, called Mode I here, involves the propagation of a sodium-filled crack driven by a cathodic deposition mechanism. In general, a significant threshold current density needs to be exceeded before the rapid Mode I fracture–degradation is initiated.

From our examinations of a number of sodium/beta-alumina electrolytes that were used in Na/S cells, it appeared that a second type of degradation was active. This mode of degradation, called Mode II here, manifests itself as a damage layer developing from the sodium side of the electrolyte. Degradation was also found to develop from the sulfur side of the electrolyte. Additionally, the usual chemical colouration propagating from the sodium electrode was also present. In this paper we first comment on the Mode I rapid breakdown and on the chemical colouration, and then discuss our observations on the Mode II progressive degradation.

2. Experimental procedures

The electrolytes used were obtained from the General Electric Research and Development Centre. They were beta-alumina electrolytes with a composition of 9.6 wt% Na_2O, 0.25 wt% Li_2O, balance Al_2O_3. The starting material was a commercial sodium/beta-alumina powder containing approximately 7.5 wt% Na_2O, with about 0.15 wt% SiO_2 as the major impurity (Alcoa-XB-2 "Superground", Aluminium Company of America, Pittsburgh, Pennsylvania). The electrolytes had been cycled in sodium/sulfur cells at current densities of approximately 100 mA cm^{-2}. The cells operated at around 300° C and were discharged as far as the two-phase region of the sodium polysulfide electrode. After cycling, the cells were cleaned with methanol and stored prior to examination in our laboratory. During storage, the cells were exposed to atmosphere for a period of about one week.

The surfaces of as-received electrolytes and of sectioned and polished electrolytes were examined by optical microscopy. It was necessary to use the staining methods described earlier by De Jonghe *et al.* [11] to reveal the flaws. The staining was carried out in a one molar aqueous solution of

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silver nitrate at a temperature of about 80° C for between 0.3 and 1.0 h. Comparisons of the electrolytes show that this staining procedure did not introduce any additional flaws that could be detected by optical microscopy. The stained electrolytes were examined using polarized light to reduce the surface scattering. Additional observations on unstained electrolytes were performed by scanning electron microscopy, high-voltage transmission electron microscopy and analytical transmission electron microscopy.

3. Results and discussion

3.1. Mode I breakdown: rapid-crack propagation

In the Mode I failure, a single sodium filled crack is propagated through the electrolyte. Once a critical flaw has been formed, propagation is rapid. The stresses arise from the Poiseuille pressure gradient generated by the flow of the sodium out of the crack. A number of difficulties remain for adequately predicting the macroscopic current densities at which the stress intensity at the sodium-filled crack tip exceeds K_{IC}, the critical stress intensity factor. Two classes of problems cause this difficulty: uncertainties in the boundary conditions, and anisotropic microstructures.

The exact calculation of the local cathodic deposition rates along the crack tip and faces is a complex problem. A first approach is the solution of the Laplacian for a particular crack geometry in a perfectly isotròpic dielectric. This yields the primary current distribution. However, the situation becomes more complicated when the flaw is actually carrying current, as has been discussed by Brennan [12]. Brennan treated the effect of electrolyte electrode interface charge-transfer resistance and local sodium pressure on the critical current densities. The problem is analogous to that of dendrite growth during cathode plating and to other electro-deposition problems such as the ones discussed by Kasper [13–15]. The same considerations should be of significance in the calculation of electrode current inhomogeneities such as those recently reported by Virkar *et al.* [16]. The uncertainties in the actual current distribution on the crack faces show up as uncertainties in the pressure distribution on the crack faces, and hence as uncertainties in K_{I} at the crack tip.

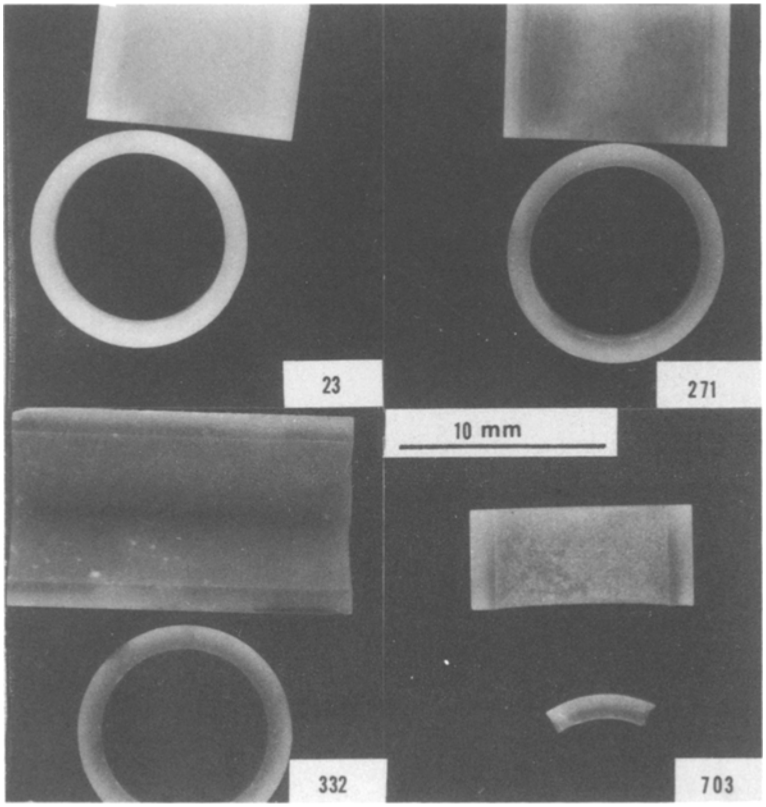

Figure 1 Silver-stained electrolytes after a total charge transfer (charge + discharge) of 23, 271, 332 and 703 A h cm^{-2}.

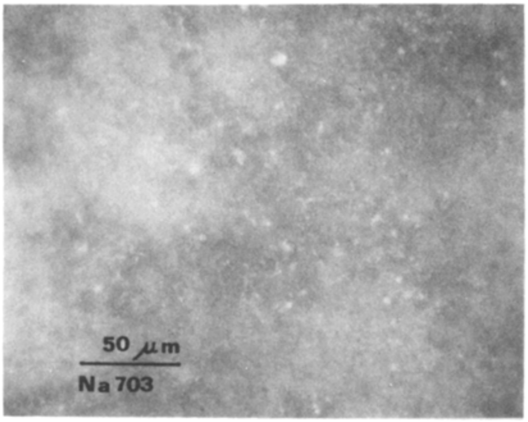

Figure 2 Silver-stained surface of electrolyte after 703 A h cm^{-2} of charge transfer, Na side. No significant features are observed.

The anisotropy of sodium/beta-alumina microstructures is perhaps an even more serious source of uncertainties. It is precisely in the initiation stage, when the critical flaws are of the order of the grain size, that microstructural anisotropy is most influential. The local microstructure will strongly affect the way in which the crack is fed. We have considered the geometries that are most effective in feeding sodium filled cracks of the order of the grain size. It appears that grain boundaries can play an important role in Mode I failure initiation, on the basis of local geometry alone [17].

3.2. Chemical colouration

It has been observed by various workers that sodium/beta-alumina darkens significantly when in prolonged static contact with sodium metal at temperatures above the melting point of sodium. This chemical darkening also proceeds in a layer-like fashion from the sodium/electrolyte interface without any current passage [18]. The chemical colouration can be enhanced very strongly if the sodium in the discoloured electrolyte is exchanged for silver by immersing it in molten silver nitrate. This discolouration was also present in the electrolytes examined and discussed here. The layer grows, however, far more rapidly than the Mode II degradation layer described below. At 300° C it has proceeded about 0.5 mm into the electrolyte after immersion in molten sodium for approximately 10 days. Transmission electron microscopy of the discoloured regions has failed to reveal any imperfections that could be attributed to the chemical darkening. This indicates that the chemical darkening is due to point defects rather than to second-phase precipitation. Experiments in this laboratory have indicated that the colouring is associated with the loss of oxygen from the electrolyte and that it introduces some electronic conductivity. The details of the experiments on chemical colouration by metallic sodium will be reported shortly.

3.3. Mode II breakdown: slow degradation

3.3.1. Sodium side

Stained sodium/electrolyte interfaces of four cells are compared in Fig. 1 after a total charge transfer (charge + discharge) ranging from 23 to

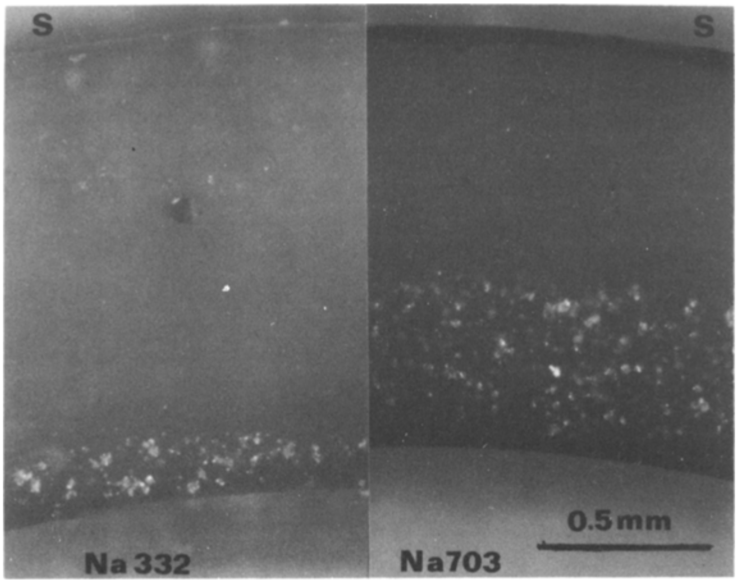

Figure 3 Damage layer progressing from the Na side of the electrolyte after charge transfer of 332 and 703 A h cm^{-2}. For the lower cycle life, the damage layer is uneven.

703 Å h cm^{-2}. A progressive though uneven darkening is observed. These surfaces were more closely examined by optical microscopy (Fig. 2), but did not reveal any resolvable features of significance. An important observation is shown in Fig. 3. In these polished and stained cross-sections it is clearly shown that significant electrolyte damage has occurred in an even layer-like fashion from the sodium/electrolyte interface. At 703 Å h cm^{-2} this layer of degradation has progressed through about one-third of the tube wall. The white, spotty reflections were found from their focusing behaviour in the optical microscope to be subsurface. They were found to be microfractures caused by internal sodium deposition. Evidence supporting this description of this mode of degradation is presented in Figs 4 and 5. Fig. 4a is a high-voltage transmission electron micrograph of a thick foil prepared by ion milling from the degraded region of an electrolyte subjected to 332 Å h cm^{-2} of charge transfer. The arrows indicate where sodium metal appears to have deposited. The deposition occurred at some grain boundaries, as well as at some grain triple junctions. Interestingly, analytical scanning transmission electron microscopy on degraded regions such as this showed that the degraded triple junctions contained silicon as well (Fig. 4b). It therefore appears that grain boundaries, as well as intergranular phases, are active in the Mode II degradation. Fig. 5 shows a microfracture area, where excess sodium as well as silicon was detected with the analytical scanning transmission electron microscope. Some of the sodium in thin foils like these may have been lost to the atmophere during foil preparation.

This slow Mode II sodium penetration cannot be accounted for by Poiseuille pressure arguments. Indeed, Mode I degradation leads invariably to rapid crack propagation.

Instead it is proposed that Mode II degradation involves electron conduction from the sodium/beta-alumina interface followed by electron-Na$^+$ recombination in the bulk of the electrolyte. The band gap for beta-aluminas is probably as high as 9 eV, and the intrinsic electronic conductivity is

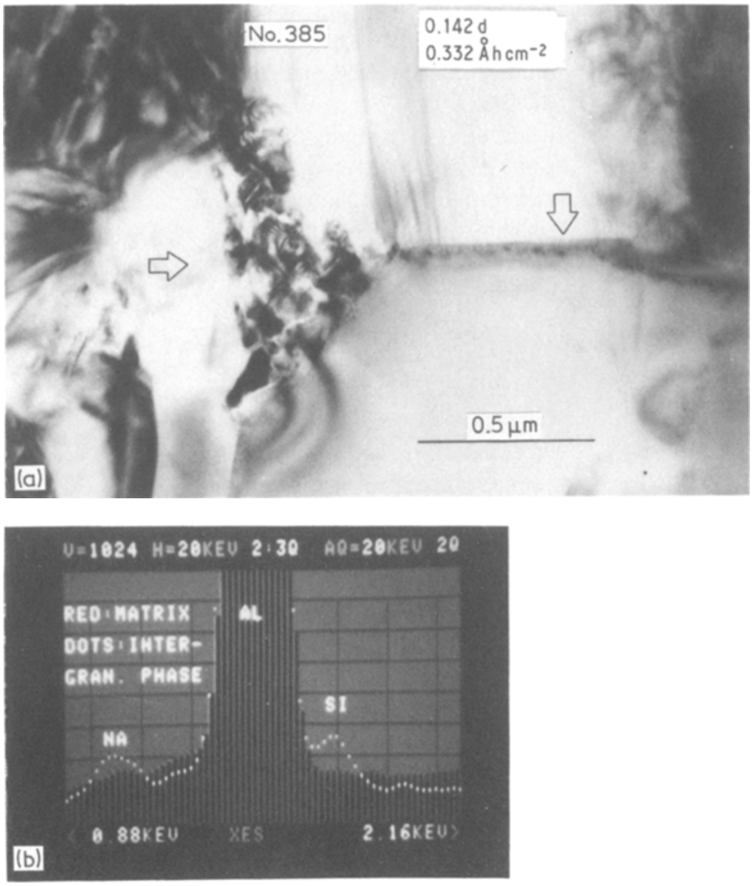

Figure 4 (a) Sodium deposits in damaged layer of electrolyte after charge transfer of 332 Å h cm^{-2}. The sodium deposits are indicated with arrows. Both grain boundaries and grain triple junctions appear involved. Thick foil observed in high-voltage transmission electron microscope to minimize loss of Na (b) analytical microscopy shows that Si is present in the triple grain junction, where extra Na has deposited.

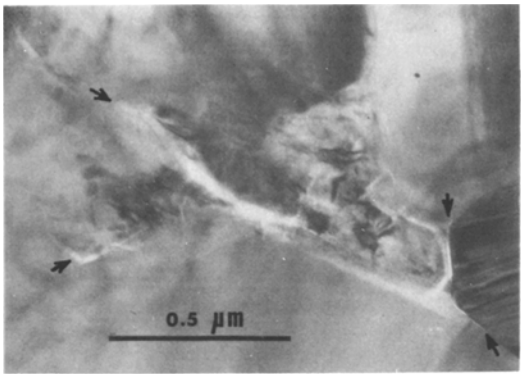

Figure 5 Thick foil prepared from damaged region of electrolyte subjected to $703\,\text{A h cm}^{-2}$ of charge transfer. Microcracks assocaited with sodium deposition are arrowed. Care needs to be exercised to distinguish these cracks from cracks introduced in foil preparation. Thick foils are necessary for avoiding interference from foil artifacts.

negligibly small at cell operating temperatures. Electrons may be injected from the Na/electrolyte interface at sufficient electric fields. However, these fields must be many times larger than the band gap. For the sodium/sulfur cells applied electric fields over the electrolyte are of the order of $10\,\text{V cm}^{-1}$ and are clearly insufficient to permit direct electron injection. Instead, the observation of internal sodium formation implies that a process has occurred that has significantly increased the electronic conductivity over its intrinsic value. The chemical colouration described in Section 3.2 is, in fact, such a process. The recombination of electrons and sodium ions in the bulk can only lead to local electrolyte microfracture if it is driven in some way by the applied voltage or the current during cell charging. A driving force for internal sodium formation can result, however, only when a gradient in electronic transport number is present or, in other words, when the electrolyte is not fully equilibrated with the electrodes. The increasing colouration that can be observed indicates that the electrolytes are indeed not in equilibrium with the electrodes, even after prolonged cell operation. The Mode II mechanism proposed here is less likely to operate in thin walled electrolytes cycled in Na/Na cells: the transport number gradient should be minimal. This would also imply that Mode II degradation involves in some way the polarization phenomena and condition of the sulphur electrode during cell operation. Microstructural and current density heterogenities, such as the ones described by De Jonghe [19] should play a role in determining where the sodium would be nucleated.

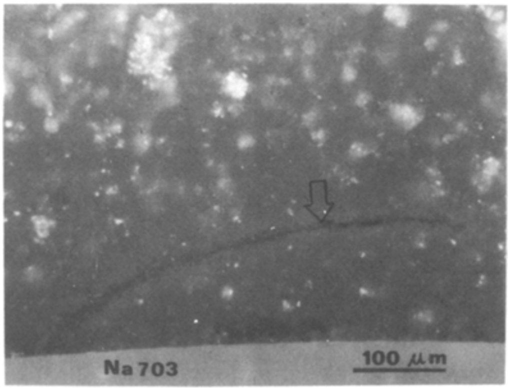

Figure 6 Mode I flaw, arrowed, in electrolyte after $703\,\text{A h cm}^{-2}$ of charge transfer. These flaws, when present, always emanate from the Na side.

Mode I flaws were also observed in cycled electrolytes. An example is shown in Fig. 6. It could not be determined at which point of the cycling life this Mode I crack had formed. It is possible that the microcracking associated with Mode II failure might actually have initiated the Mode I failure. It is interesting to note that the Mode I crack shown in Fig. 6 did not remain perpendicular to the tube walls. We attribute this deflection to a basic instability in the Mode I geometry; a deflected crack is more effectively current-fed. This deflection can clearly lead to spalling of the electrolyte surfaces. Similar crack deflections have been observed by us in accelerated sodium/sodium testing of electrolyte tubes at 300° C [20].

3.3.2. Sulfur side

Degradation was observed on the sulfur side of the used electrolytes as well. A macrograph comparing the four examined electrolytes is shown in Fig. 7. At short cycling times, the sulfur/electrolyte surface is virtually unaffected. At long cycling times a significant degradation occurs, as shown in Fig. 8a and b. Fig. 8a clearly shows the "imprinting effect" that has been reported by other workers as well [21]. The light and dark regions in the electrolyte surface reflect the macrostructure of the graphite filler that was used to facilitate current extraction from the positive sulfur electrode. The decoration of these surfaces, with the method described earlier, revealed the presence of surface cracks (Fig. 8b). A cross-section of the electrolyte

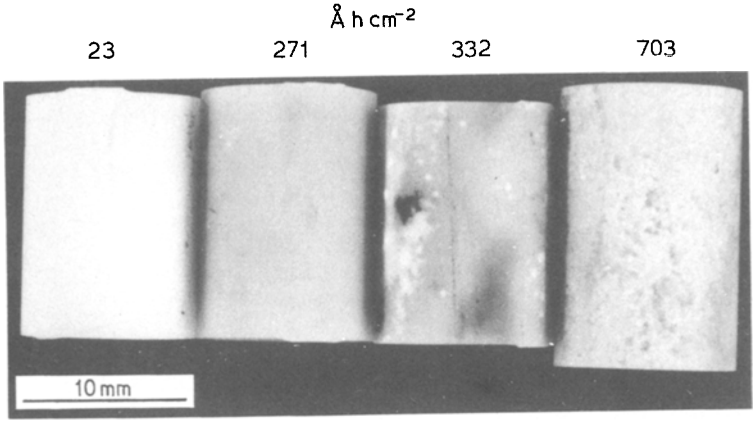

Figure 7 Comparison of the four electrolytes after staining; sulfur sides after indicated charge transfers.

at the positive electrode is shown in Fig. 9. Again, a band of degradation is observed after extensive charge transfer. This layer appears quite non-uniform at low-charge transfer, but it is fully established after 703 Å h cm^{-2}. Scanning Auger microscopy indicated the presence of some sulfur in this layer. The degradation of the sulfur side of the electrolyte is, at present, not understood. Since it is associated with the "imprinting effect", it is also due to current passage.

4. Conclusions

A second mode of degradation has been observed in sodium/beta-alumina solid electrolytes cycled in sodium/sulfur cells. This Mode II degradation propagates as a damage layer from the sodium/electrolyte interface. It is distinguished from the Mode I failure, which consists of isolated cracks propagating from the sodium side and from the chemical discolouration. Mode II degradation appears to involve grain boundaries, as well as intergranular phases. The observations led to the postulate that the slow degradation could be attributed to electron conduction and recombination during the charging cycle of the sodium/sulfur cell.

Degradation also developed on the sulfur side of the electrolyte. This degradation is associated with the carbon felt "imprinting effect" and is also the result of current passage through the electrolyte.

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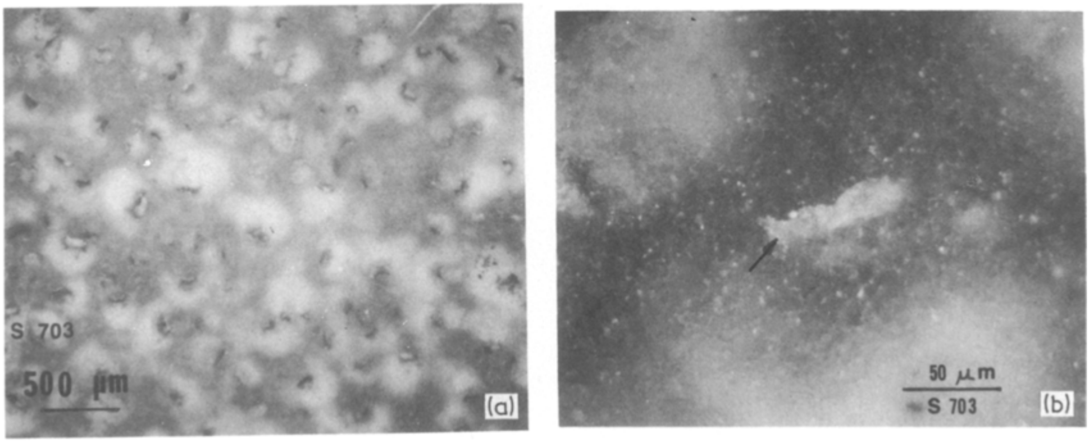

Figure 8 (a) "Imprinting" effect of graphite fibre filler on S side of electrolyte (b) the silver staining shows surface cracks associated with this imprinting. Electrolyte subjected to charge transfer of 703 Å h cm^{-2}.

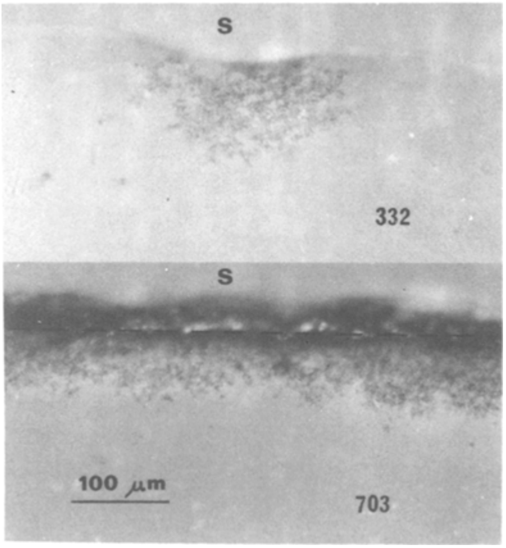

Figure 9 Degradation of sulfur side of electrolyte after 332 and 703 A h cm^{-2}, after silver staining. The degradation layer becomes more uniform after prolonged electrolysis.

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