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A supersaturation model for the degradation of sodium β/β''-aluminas

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A mechanism is proposed for the sodium degradation of β/β'' alumina electrolytes. It is based on the Na^+ supersaturation of feeder grains peripheral to flaws in the liquid-sodium/electrolyte interface. This supersaturation is brought about by the focusing of the current by the flaw and leads to local oxidation of oxygen ions in the aluminate structure. This process leads to the formation of colour-centres and sodium atoms in the grains. The latter coalesce to form sodium colloids, microcracking the microstructures. These microcracks join the originating flaw and promote its extension. A model is presented which demonstrates the feasibility of the proposed degradation mechanism and it is discussed in light of other associated physical phenomena.

1. Introduction

One of the major hurdles remaining in the commercialization of the Na/S high-energy-density battery is the degradation of the ceramic electrolyte by sodium dendritic growth through its section. The popular explanation of this phenomenon is based on the development of pressure (Poiseuille pressure) in electrolyte surface flaws on the sodium (liquid) electrode side. This pressure, it is suggested, is the result of the discharge of more sodium into these flaws than can escape into the bulk electrode during the charging process. On a postmorten basis this seems a logical explanation. Sodium dendrites extend by flaw propagation under the influence of the internal pressure. A number of associated phenomena negate this explanation and the model developed in the present paper, proposes sodium dendrite development by sodium precipitation in the ceramic microstructure local to the current-focusing surface flaws. These precipitates join the main flow via the microcracks they induce. This explanation is based on the proposal of De Jonghe *et al.* [1] who defined mode I and mode II types of degradation. The feasibility of the model here proposed is demonstrated by considering the influence of the atomic structure and the microstructure of the two common polymorphs of β-Al_2O_3 (β- and β''-) on the degradation process. It is further shown that the proposed explanation agrees in general with the physical processes observed to accompany sodium degradation of β/β''-Al_2O_3 electrolytes.

2. The electrolyte material

β-Al_2O_3 exists in two polymorphs designated β and β''. Both compounds are nonstoichiometric with respect to the alkali content, having composition ranges $9\,Al_2O_3$–$11\,Al_2O_3$ and $5\,Al_2O_3$–$6\,Al_2O_3$ for β and β'', respectively. This nonstoichiometry is balanced by intrinsic (O_i) or extrinsic $(Li_{Al})''$ or $(Mg_{Al})'$ defects. Al^{3+} and O^{2-} ions are packed into cubic spinel formation into what are termed "spinel-blocks". Two such blocks constitute the unit cell of β-Al_2O_3. The unit cell base is at $c_0 = 1/2$ of a spinel-block with a full block occupying the central position and the cell being completed by another half block of Al–O. The blocks are separated by alkali-containing planes and in the β-Al_2O_3 case, these are mirror planes for the spinel blocks. Monovalent ions can only move in these planes and their mobility through the spinel blocks is about 10^{-6} times that in the mirror planes.

These mirror planes are maintained "open" by oxygen ion "props" and, as these have an ionic

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radius of 0.14 nm and that of Na^+ is 0.098 nm, the alkali ion is highly mobile on the mirror or "conduction" plane.

The crystallographic position of the propping O^{2-} ion is 0(5). The oxygen planes constituting the "floor" and the "ceiling" of the conduction plane are close packed and 0.25 of the possible octahedral interstices between these close packed planes are occupied by 0(5) ions (O–O distance = 0.554 nm). There are three possible Na^+ sites on these planes; the octahedral site in the centre of the 0(5)-triangles (so-called Beever–Ross or BR site), the octahedral site between two 0(5) ions (the mid-oxygen position (MO)) and in two-coordination between two mirrored oxygen ions (so-called anti-Beever–Ross site (ABR)) again in the centre of 0(5) triangles. This third site is the least favourable for Na^+ in the β–Al_2O_3 structure. The distance centre-to-centre of the mirror oxygen ions is 0.476 nm. This compares with the diameter of Na^+ approximately 0.20 nm plus that of O^{2-} (= 0.28 nm), i.e. 0.48 nm. The proximity of these values led Beever and Ross to reject this position. In β-Al_2O_3 the Na^+ diffusion path is from BR to MO to ABR to MO to BR positions and the ABR bottleneck rate-controls the diffusion process. Now β-Al_2O_3 is always nonstoichiometric with excess Na^+; the defect equilibrium is thought to be [2];

$$(2Na_i^+)^{\cdot\cdot} = (O_i(5))''.$$

The O_i occupy empty 0(5) positions further inhibiting the mobility of Na^+ on the conduction plane.

β''-Al_2O_3 has a three spinel block unit cell. This symmetry eliminates the mirror plane and so no ABR sites exist. Three conduction planes exist in the β''-Al_2O_3 unit cell and the number of Na^+/unit cell is higher (6.66 as compared to 2). The unit cell is also of larger volume. These two factors together with the relaxation of the ABR bottleneck, increases the diffusivity of Na^+. The Na^+ over-stoichiometry in the β''-Al_2O_3 case is controlled by;

$$(Li_{Al})'' = 2(Na_i)^{\cdot}$$

and/or

$$(Mg_{Al})' = (Na_i)^{\cdot}$$

In fact Li^+ and/or Mg^{2+} are requisite to stabilize the β''-Al_2O_3 phase. The interfering $O_i(5)$ ions are not present in the β''-Al_2O_3 structure.

The diffusivity of Na^+ in β-Al_2O_3 is about $10^{-4}\,cm^2\,sec^{-1}$ at 300° C. For β''-Al_2O_3, D_{Na} (300° C) = $10^{-3}\,cm^2\,sec^{-1}$. Clearly β''-Al_2O_3 is the most desirable phase for high conductivity but it is the least thermally stable.

The mirror or conduction planes of β/β''-Al_2O_3 constitute cleavage planes so the mineral has a plate-like morphology. This is clearly shown in individual grains of the polycrystalline electrolyte. Realizing that Na^+ can only move along these cleavage planes, it is evident that much of the microstructure will be Na^+-blocking (misaligned grain boundaries) [3]. In terms of the discharge of sodium into a surface flaw, only a fraction of the grains periferal to the flaw will be orientated so as to be capable of passing Na^+ into the flaw. This fact will be considered in more detail later.

3. β/β'' – alumina degradation in sodium environments

The following physical observations are generally agreed to accompany the degradation of β-Al_2O_3 electrolytes in sodium environments; degradation initiates at the liquid-sodium/electrolyte interface; it progresses through the ceramic at a constant rate for a given current density and a critical current density exists above which degradation proceeds apace; it accompanies the charging cycle of the Na–S battery and blackening (or discolouration) is always observed to accompany degradation; current passage is not necessary for discolouration, immersion in liquid sodium will blacken the electrolyte; the grain size of the polycrystal plays little or no role in the degradation kinetics, but the initial strength does and polishing the surface of the electrolyte reduces degradation. In a companion paper the influence of applied stress on the degradation kinetics was reported [4]. It was found that applied stress of either sign increased the degradation rate and lowered the critical current density requisite for fast degradation. Degradation increases with increasing temperature and the rate-controlling process appears to be the diffusion of Na^+ in the ceramic electrolyte [4]. Observations pertinent to the discolouration are that it occurs with no passage of current; the TEM failed to identify the originating defects [5]; careful polishing reveals it to be deep violet [6]; sodium colloids, microcracks and some macrocracks are observed after extended service [1]; high-resolution electron microscopy shows the possible destruction of conduction layers and the "sweating" out of sodium metal from foils [7–10] and ESR detected two centres in the discoloured region, one associated with an unpaired electron bonded to an aluminate lattice site and one interpreted as colloidal sodium of 1 μm diameter [11]. Similar blackening has been observed in the other oxide systems and its appearance in ZrO_2 at high current densities is associated with zirconium colloids [12].

Surface flaws in the sodium liquid/electrolyte interface play a significant role in the degradation process. Armstrong *et al.* [13] cycled Na/Na, β-Al_2O_3 cells using electrolyte pellets with varying grades of surface polish. They noted that the electrolyte with the highest polish (1 μm diamond) gave the best lifetime. It is, therefore, likely that surface flaws do focus the passing current.

The Poiseuille-pressure models of degradation consider that more sodium is discharged than can be transferred out of the flaw to the bulk electrode. Such a transfer is controlled by the viscosity of liquid sodium which should decrease with increasing temperature. The deterioration should decrease with temperature therefore, but it is observed to increase. Virkar has raised the question of the relevance of bulk viscosity to that of a liquid in microscopic cracks [14] but, notwithstanding this objection, if the values of stress intensity factor at the flaw tip are calculated using the Poiseuille pressure (P) relationship developed by Virkar [14] and the simple $K_{Ic} = P(\pi a)^{1/2}$ relationship then, for a 20 μm flaw in the surface of a ceramic maintaining current density of $0.5\,A\,cm^{-2}$, $K_I = 0.24\,MPa\,m^{1/2}$ and for a current density of $2.5\,A\,cm^{-2}$, $K_I = 0.36\,MPa\,m^{1/2}$. K_{Ic} values for β/β''-Al_2O_3 ceramics range between 4 and $6\,MPa\,m^{1/2}$ [4], well in excess of values developed by Poiseuille pressures.

The superimposition of applied stresses on the electrolysing system [4] was rationalized on the basis of combatting Poiseuille pressure and extending the electrolyte life. Compressive applied stress should achieve the desired result but in fact the lifetime was reduced and the critical current density lowered. The temperature dependence of the deterioration, the low K_I values developed and the impotence of applied compression, all suggest that the Poiseuille pressure degradation model is inappropriate. Further to this, values of critical current density based on models of Poiseuille pressure development give unreasonable results ($1500\,A\,cm^{-2}$ [15]; $12\,400\,A\,cm^{-2}$ [14]). In defence of these values, Virkar *et al.* [16] pointed out that nonwetting of the electrolyte by the liquid sodium could induce such high current densities around the perifery of the non-wetted areas.

Recently, De Jonghe *et al.* [1] have suggested that two modes of β-Al_2O_3 electrolyte degradation occur in sodium environments.

Mode I – crack propagation in the ceramic due to the egress of sodium liquid out of surface flaws on the sodium electrode side being slower than the ingress of sodium [1] into the flaw.

Mode II – the local reaction of the Na^+ concentrated by the flaws in the sodium/electrolyte interface with ionic species in the ceramic to produce colloidal sodium and point defects.

The Ford workers [17] noted that blackening occurs with no current passage and, following 10 days immersion at 300° C in liquid sodium, a darkened layer of 0.5 mm thickness develops. De Jonghe *et al.* suggested that the colouration is associated with oxygen loss. They also noted that some electronic conductivity developed. Extended times of service were observed to result in sodium colloids and microcracks in the discoloured layer and, in some cases, Mode I cracks were observed therein. Microcracks and pitting were also observed by Powers *et al.* [18] in regions of heavy blackening. These observations suggest the following reaction sequence;

$$Na^+ + O(5) \rightarrow Na + O + V'_{Na} + (e)^{\cdot}_{O}$$

where Na^+ is a sodium ion on a sodium site, O(5) is the conduction plane oxygen ion, O is an oxygen atom and V'_{Na} is a vacant sodium site. $(e)^{\cdot}_{O}$ is an electron trapped at an O(5) site. Effective charges are superscripted using Kröger–Vink notation. In air the oxygen atom produced can react with the sodium atom to give Na_2O [19] or dissolve in the liquid sodium colloids. In high vacuum (as in the TEM for example), the oxygen may escape as $1/2\,O_2$ giving the free metallic sodium observed. The reaction creates colour centres $(e)^{\cdot}_{O}$, the free electron detected by ESR, and will lead to the violet colour or darkening of the electrolyte and collapse of the conduction planes as O(5) are removed. The fact that the darkened electrolyte has been observed to maintain its conductivity suggests that initially the removal of O(5) does not cause the conduction plane collapse or substantial electronic conductivity. The darkening does herald the onset of degradation but, as long as the current density is maintained at a subcritical level, no ionic conductivity deterioration occurs. It is suggested that above the critical current density value, sufficient O(5) ions are removed to cause conduction plane collapse and accelerated degradation ensues (as observed). The ease with which these reactions occur is evidenced by the darkening of the electrolyte by sodium immersion alone. The sodium atoms coalesce to sodium or Na_2O colloids and restrictions of the dense microstructure result in concomitant microcracking. These microcracks will extend back to the original focusing flaw to give sodium "dendrite" growth. Increased electronic conductivity could result from $(e)'_O$ and sodium. That these restrictions are not rate-controlling is evidenced by the apparent control by Na^+ ion diffusion [4].

The accelerated degradation under stresses of both sign and the differential between the higher and lower strength materials can be explained in terms of the sodium precipitation. Both stresses will reduce the material back-stress opposing precipitation but on planes and boundaries of different orientation, i.e. applied compressive stresses will lower the resistance to precipitation on planes and boundaries parallel to the applied stress axis; applied tensile stresses will lower the backstress on planes perpendicular to the applied stress axis. De Jonghe *et al.* [5] observed sodium precipitates on the planes and boundaries of degraded electrolytes in the vicinity of the sodium electrode. The backstress opposing such precipitation will be a function of the pristine strength of the electrolyte so producing the observed material differentiation.

The feasibility of the supersaturation of Na^+ sites in grains periferal to an Na-liquid-filled flaw remains to be demonstrated. The basic premise is that, if Na^+ ions arrive at conduction-plane sites faster than they can be diffused on and discharged, supersaturation will occur and the reactions will be favoured.

4. Model

Evidently Na(l)-surface flaws are important and a 20 μm flaw will be considered. It will be assumed that the average grain size is also 20 μm and that the flaw influences the Na^+ diffusion within those grains that intercept it, i.e. the Na^+ ions see single crystal discharge paths to the sodium(liquid) in the flaw and the flaw influences one grain-size distance from its tip. Assume the flaw is of unit depth and it focuses the current within a volume of the shape shown in Fig. 1. The flaw focuses the current by reason of its closer proximity to the anode. As the cathode is approached the focusing power of the flaw diminishes giving the triangular prism shape of influenced-volume for the body of the flaw (the focusing of current by the sides of a flaw was first suggested by Brennan [20] and the decreasing influence in the proximity of the cathode was also assumed by Virkar [14]). The flaw tip is the most powerful focusing location and its sphere of influence is shown as a hemicylinder. Not all the grains periferal to this flaw are suitably oriented to discharge Na^+ into the flaw. As both β- and β''-Al_2O_3 are two-dimensional conductors of Na^+, those periferal grains whose conduction planes do not intercept the flaw surfaces cannot transfer Na^+ into the flaw. Considering a line intersection with the flaw top (or bottom) surface, a hemicylinder of

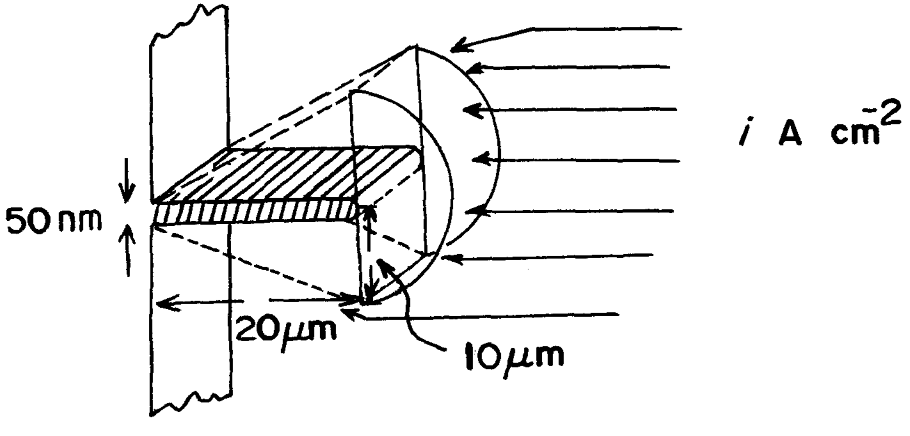

Figure 1 Model for flaw-focusing volume. Surface area of flaw influence = 900 μm^2.

TABLE I Available sites in β- and β''-Al_2O_3 and number of atoms discharging

i (A cm^{-2})	i_{focus}	Number of moles of sodium	Number of atoms of Na^+	Number of empty sites	
				β-Al_2O_3	β''-Al_2O_3
0.5	4.5×10^{-6}	0.466×10^{-11}	2.76×10^{12}	0.8×10^{12}	1.6×10^{12}
1.0	9×10^{-6}	0.93×10^{-11}	5.58×10^{12}	0.8×10^{12}	1.6×10^{12}
1.5	13.5×10^{-6}	1.39×10^{-11}	8.34×10^{12}	0.8×10^{12}	1.6×10^{12}
2.0	18×10^{-6}	1.86×10^{-11}	11.2×10^{12}	0.8×10^{12}	1.6×10^{12}
2.5	22.5×10^{-6}	2.3×10^{-11}	14.0×10^{12}	0.8×10^{12}	1.6×10^{12}

conduction plane–line intersections are possible but only half of this hemicylinder of planes is in the positive potential-drop direction. Those planes intercepting in the negative direction cannot discharge Na^+ in opposition to the current flow. Hence, about 50% of the grains periferal to the flaw cannot discharge Na^+ into it. This figure will be $< 50\%$, for those grains with conduction planes parallel to the flaw (the base of the hemicylinder) cannot discharge Na^+ into it. A further reduction of feeder grains is associated with the number of grains of β-Al_2O_3 phase periferal to the flaw. These have a lower conductivity, i.e. are narrower pipes, and constitute a restriction to Na^+ discharge. For a fraction of β-Al_2O_3 phase of 0.2 in the microstructure, 80% of the quarter-cylindrical feed volume is β''-Al_2O_3 grains, i.e. 40% of the periferal grains are β''-Al_2O_3 correctly oriented with respect to current flow and flaw-conduction plane interception. Considering these reductions, it will be assumed that 33% of the grains constituting the perifery of the flaw are suitably oriented to discharge Na^+ into it.

The surface area of the flaw-influenced volume is about 900 μm^2 for the flaw dimensions assumed. If a current density of 0.5 A cm^{-2} passes through the electrolyte, the current focused on the surface of the flaw-influenced-volume is;

$$\left(\frac{0.5 \times 900}{10^8}\right) \text{A} = (45 \times 10^{-7})\text{A}.$$

In terms of moles of sodium discharged into the crack this is;

$$\left(\frac{45 \times 10^{-7}}{96\,500}\right) = 5 \times 10^{-11} \,\text{mol sec}^{-1}$$

$$= 30 \times 10^{12} \,\text{atoms sec}^{-1}.$$

The Na^+ ions feed down the β/β''-Al_2O_3 conduction planes and these are 1.12 nm apart. The number of conduction planes feeding the flaw surface is

$$\left(\frac{2 \times 20 \times 0.05 \times 0.33}{11.2 \times 10^{-4}}\right) + \left(\frac{2 \times 20 \times 0.33}{11.2 \times 10^{-4}}\right)$$

$$+ \left(\frac{0.33 \times 0.05}{11.2 \times 10^{-4}}\right) = 1.23 \times 10^4$$

(the first term is associated with the sides of the flaw (50 nm apart); the second term is the area of the top and bottom of the flaw and the third the area of the flaw tip. The number of planes into the flaw tip is determined by the flaw tip area (assumed 0.05 μm diameter); one third of conduction planes are assumed available for Na^+ discharge). The total area of these planes in 20 μm-grains of unit depth will be;

$$20 \times 1.23 \times 10^4 \,\mu m^2.$$

The basal plane area of the β/β''-Al_2O_3 cell is about 0.30 nm^2 (MO positions 0.558 nm apart) and this area contains two possible Na^+ sites in β-Al_2O_3, i.e. a BR and an MO and three in β''-Al_2O_3. The total number of available sites for Na^+ in β-Al_2O_3 is thus;

$$\frac{25 \times 10^4}{30 \times 10^{-4} \times 10^{-4}} \times 2 = 1.6 \times 10^{12}.$$

In stoichiometric β-Al_2O_3, half these sites contain Na^+ hence, the number of empty sites $= 0.8 \times 10^{12}$. In stoichiometric β''-Al_2O_3 two of the three sites are occupied. The number of available sites in β- and β''-Al_2O_3 and the number of atoms of sodium discharging, for the series of current densities, are shown in Table I. It should be pointed out that stoichiometric β- and β''-Al_2O_3 are assumed in the calculation. In fact both phases contain excess Na^+ so the number of available sites will be less in each case.

Clearly the possibility exists that the sites could become saturated. Considering the diffusivity of Na^+ in both structures [21]

$$(D_{Na})_{\beta\text{-}Al_2O_3}(300° \text{C}) = 2.39 \times 10^{-4} \,\text{cm}^2\,\text{sec}^{-1}$$

$$(D_{Na})_{\beta''\text{-}Al_2O_3}(300° \text{C}) = 1 \times 10^{-3} \,\text{cm}^2\,\text{sec}^{-1}.$$

TABLE II Number of Na^+ ions as a function of current density

i ($A\,cm^{-2}$)	Number of Na^+ ions (300° C)	β''-Al_2O_3 Na^+ (300° C)
0.5	$(2.76 \times 10^{12} \times 0.16 \times 10^{-5}) = 0.44 \times 10^7$	0.22×10^7
1.0	0.90×10^7	0.44×10^7
1.5	1.34×10^7	0.67×10^7
2.0	1.8×10^7	0.9×10^7
2.5	2.24×10^7	1.12×10^7

The Einstein diffusion (D)/distance (x) relationship, $x = 2(Dt)^{1/2}$, gives that Na^+ diffuses 308 $\mu m\,sec^{-1}$ in β-Al_2O_3 and 612 $\mu m\,sec^{-1}$ in β''-Al_2O_3, at 300° C. The number of sites in 308 μm (assuming sites are 0.5 nm apart) is 6×10^5 giving a calculated site residence time (relaxation time) of 0.16×10^{-5} sec. Now as the current density increases, the number of Na^+ arriving at the perifery increases and the question arises, have Na^+ ions one site immediately ahead of the Na^+ ions just arriving, moved, i.e. have too many arrived for the just-vacated sites to accommodate. The number of planes feeding the flaw is 1.23×10^4. Taking the first sites of these planes (assumed 1 μm width), the number of sites at the exit lines into the flaw are $0.2 \times 10^4 \times 1.23 \times 10^4$, i.e. 2.4×10^7 and these empty in 0.16×10^{-5} sec. In this time the number of Na^+ arriving as a function of current density is shown in Table II for β/β''-Al_2O_3 at 300° C.

Comparing these values with the number of sites available for these ions, the sites in β-Al_2O_3 approach saturation at 2.5 $A\,cm^{-2}$ at 300° C and those of β''-Al_2O_3 are below the saturation condition. Three factors which could change the latter situation are; the channelling of excess Na^+ arriving at saturated β-Al_2O_3 grains to their β''-Al_2O_3 neighbours (a condition made more severe if O(5) oxidation occurs and conduction planes collapse); impurities in the system "blocking" the conduction planes via the mixed ion effect and site occupation and the decreased number of available sites due to nonstoichiometry.

5. Discussion

The model demonstrates the feasibility of the ionic supersaturation of the periferal grains to an Na-interfacial flaw by the current focusing power of the flaw. It also explains the observed control of the degradation process by the diffusivity of Na^+. The critical current density value requisite for the degradation mechanism suggested is 2.5 to 3 $A\,cm^{-2}$. This value is close to that reported for stress-free β/β''-Al_2O_3 ceramics [4]. That the O(5) oxidation reaction occurs easily, is supported by the darkening of β/β''-Al_2O_3 on immersion in liquid sodium. The ease of these reactions also removes the problem of supersaturation polarization. Such polarization would result in a back e.m.f. and a cessation of flow of Na^+ into the flaw region. Clearly sodium atoms can be produced within the electrolyte, with accompanying colour centres, by oxidation of oxygen ions in the aluminate structure. It is suggested that the O(5) oxygen is oxidized. Evidence for this is the concurrent collapse of conduction planes and the appearance of sodium metal during foil observation by high-intensity TEM. Much has been made in the literature of the role of metal impurities (K^+, Ca^{2+}, Si^{4+}, H_3O^+) in accelerating the degradation process [6, 17, 22, 23]. Rassmussen *et al.* [6] demonstrated that Ca^{2+} is much more detrimental than K^+. Foster *et al.* [24] found the mixed ion effect in Na–K β-gallate (isomorphous with β-Al_2O_3) led to a discontinuous decrease in the alkali-ion conductivity for a particular K/Na ratio.

If K^+, Ca^{2+}, H_3O^+ penetrate the surface layers of the electrolyte clearly an isopleth of critical alkali-ion ratio can occur and the conductivity (or diffusivity) of alkali ions at the location will be drastically reduced. The maintenance of the applied current density and the increased ionic resistivity must require electronic conduction, which can occur via $(e)'$ and sodium metal. Such increased ionic resistivity will catalyse the suggested reaction sequence and the mechanism of accelerated degradation can be understood in terms of the suggested model. Clearly the model is conservative and supersaturation is a distinct possibility in both the β- and β''-Al_2O_3 phases.

A pertinent analogy to illustrate the proposed mechanism and its juxtaposition to that of Poiseuille pressure failure is the "Star-Wars disturbance". The village charity obtained "Star-Wars" and, intending to maximize the return, chairs were placed in close rows to fill the hall from back to front. To minimize the time of audience replacement, the new audience entered simultaneously with the exit of the old, i.e. as the previous audience left through back-exit doors on the right, the new audience entered through doors on the left. As a seat was vacated, a new viewer filled it. A blockage occurred in the system and the orderly array of chairs was destroyed. Poiseuille-pressure advocates suggested the exit doorway was too narrow and the old audience had restricted exit resulting in chair upheaval. The present model suggests the inflow rate of the new audience was too high and overturned chairs resulted from supersaturation of the entrance aisles. Overturned chairs in the "conductivity" aisles compounded the problem and damage resulted.

6. Summary

A model is presented for the degradation of β/β''-Al_2O_3 electrolytes in sodium environments. The recognized physical characteristics of the material during degradation are incorporated. The model predicts that sodium ion diffusion rate-controls the degradation process and that a critical current density of about $3\,A\,cm^{-2}$ will lead to accelerated degradation. Both of these predictions agree with experimental observations [4].

It is suggested that more Na^+ ions are focused into grains periferal to flaws that can be transmitted by those grains. The result is localized oxidation of oxygen O(5) ions to give sodium atoms, electrons trapped at oxygen sites (colour centres), the eventual collapse of the conduction planes by removal of the O(5) ions spaced between the structural spinel blocks and the onset of electronic conduction. It is further suggested that the sodium atoms coalesce into colloids and the dense micro-structure is microcracked as a result. These micro-cracks facilitate further sodium precipitation which joins the main flow giving a sodium "dendrite" progressing through the electrolyte section. The feasibility of the "supersaturation" concept is demonstrated for β/β''-Al_2O_3 at 300° C.

One problem remains unanswered, i.e. the longevity of Na/Na cells *vis-à-vis* Na/S cells. It is possible that this observation is associated with impurity ions in the sulphur side of the Na/S cells. The purity of the sodium electrode has received much attention [6] but investigations of the presence of K^+, Ca^{2+}, etc. in the sulphur and/or the metal containment vessel seem to have been overlooked.

References

1. L. C. DE JONGHE, L. FELDMAN and A. BEUCHELE, *J. Mater. Sci.* **16** (1981) 780.
2. W. L. ROTH, *J. Solid State Chem.* **4** (1972) 60.
3. L. C. DE JONGHE, *J. Mater. Sci.* **14** (1979) 33.
4. K. KURIBAYASHI and P. S. NICHOLSON, *ibid.* **18** (1983) 1590.
5. L. C. DE JONGHE, L. FELDMAN and P. MILLETT, *Mater. Res. Bull.* **14** (1979) 589.
6. J. R. RASSMUSSEN, G. R. MILLER and R. S. GORDON, Abstract No. 720, *Ann. Conv. Electrochem. Soc.* (Montreal, May, 1982).
7. J. O. BOVIN, *Nature* **273** (1978) 136.
8. *Idem,* in "Fast Ion Transport in Solids", edited by P. Vashishta, J. N. Mundy and G. K. Shenoy (Elsevier North Holland Inc., 1979) p. 315.
9. T. B. TANG, G. ABRAMSON and M. M. CHANDHRI, *Solid State Ionics* **3/4** (1981) 397.
10. V. MATSUI, *ibid.* **3/4** (1981) 135.
11. D. GOURIER and A. WICKER, Abstract No 722, *Ann. Conv. Electrochem. Soc.* (Montreal, May 1982).
12. P. FABRY, M. KLEITZ and C. DEPORTES, *J. Solid State Chem.* **6** (1973) 230.
13. R. D. ARMSTRONG, T. DICKINSON and J. TURNER, *Electrochim. Acta* **19** (1974) 187.
14. A. V. VIRKAR, *J. Mater. Sci.* **16** (1981) 1142.
15. D. K. SHETTY, A. V. VIRKAR and R. S. GORDON, "Fracture Mechanics of Ceramics" Vol. 4, edited by R. C. Bradt, P. D. H. Hasselman and F. F. Lange (Plenum Press, 1978) p. 651.
16. A. V. VIRKAR, L. VISWANATHAN and D. R. BISWAS, *J. Mater. Sci.* **15** (1980) 302.
17. N. WEBER, T. COLE and T. K. HUNT, *Bull. Amer. Ceram. Soc.* **59** (1980) 377.
18. R. W. POWERS, M. W. BRECHER and P. S. PARK, Abstract No. 725, *Ann. Conv. Electrochem. Soc.* (Montreal, May 1981).
19. L. C. DE JONGHE, *J. Electrochem. Soc.* **129** (1982) 752.
20. M. P. J. BRENNAN, *Electrochim. Acta* **25** (1980) 629.
21. J. T. KUMMER, *Prog. Solid State Chem.* **7** (1972) 141.
22. J. FALLY, C. LASUE, Y. LAZENNEC and P. MARGOTINE, *J. Electrochem. Soc.* **120** (1973) 1292.
23. S. N. HEAVENS, *J. Mater. Sci.* **17** (1982) 965.
24. L. M. FOSTER, M. P. ANDERSON, G. V. CHANDRASHEKHAR, G. BURNS and B. B. BRADFORD, *J. Chem. Phys.* **75** (1981) 2412.

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