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MICROSTRUCTURE, DEFECTS, AND SODIUM TRANSPORT IN SODIUM BETA-ALUMINA

SOLID ELECTROLYTES

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In this paper, some imperfections are discussed, including point defects, non-stoichiometry due to Na₂O loss, planar defects and grain boundaries. Their relationship to fast ion transport is indicated. For most cases studied to date, only qualitative relationships between defects and ionic conductivity can be given.

Introduction

Sodium beta-aluminas are rapidly becoming some of the most studied materials. In spite of the attention that these solid electrolytes have received from the material science, the solid state physics, and the electrochemical community, many problems remain unanswered. In particular, the nature of the charge compensating defects for excess sodiums, the diffusion of ions in highly defective systems, and the initiation of electro-chemical degradation need to be clarified further. For charge compensation, so far only the oxygen interstitial with two associated aluminum ion Frenkel pair \(^1\) has been clearly shown to be present. It is, however, possible that other charge compensating defects in sodium beta-alumina are of importance as well. \(^2\) Other microstructural features and
defects such as planar disorder in 00.1 direction and antiphase type boundaries\textsuperscript{3} or complex faults,\textsuperscript{4} grain boundaries,\textsuperscript{5, 6} etc., have been studied in beta-alumina, but to date, only qualitative relationships between those imperfections and sodium ion transport can be given. Of additional importance in sodium ion transport through solid electrolytes are the polarization effects that can occur in the electrolyte at the electrode/electrolyte interfaces. Accumulation at these interfaces of impurities originating from cell corrosion processes may be expected to make the electrode/electrolyte interface less and less reversible as time proceeds. Therefore, increasing polarization phenomenon may occur that eventually could lead to initiation of electrolyte breakdown. In this paper, we will discuss some aspects of non-stoichiometry involving Na\textsubscript{2}O loss from the electrolyte during fabrication. Further, microstructural defects including complex faults, 00.1 disorder and heterophase intergrowth will be reviewed, and role of grain boundaries in the conduction process will be discussed.

1) Non-stoichiometry, Soda Loss

It has now been well established that sodium beta-alumina can exist over an appreciable range of non-stoichiometry. Recently, it was reported that a nearly stoichiometric sodium beta alumina, Na\textsubscript{Al\textsubscript{11}}O\textsubscript{17}, could be prepared by a decomposition and exchange process starting from ammonia beta-alumina.\textsuperscript{7} The sodium rich limit of sodium beta-alumina has not been established with great accuracy, but is generally believed to be around \textit{x} = 0.3 for the chemical formula (1 + \textit{x}) Na\textsubscript{2}0.11 Al\textsubscript{2}O\textsubscript{3}. It should be emphasized that the problem is complicated by the fact that sodium beta-alumina can have non-stoichiometry that is not thermodynamically stable, and that the presence of crystallographically closely related aluminates with different sodium content cannot always be readily detected.
Once a material has been prepared, sodium can be lost from it. This involves Na₂O loss from the surface at high temperatures.

The process of soda loss appears to have slightly different crystallographic consequences for beta and for beta"-alumina. In beta"-alumina, soda loss leads to the elimination of nearly all oxygens in the conduction plane, which leads to the collapse and subsequent shear of the lattice to a spinel-like structure. A lattice image of such a shear fault that was seen to form in the transmission electron microscope due to Na₂O loss to the microscope atmosphere is shown in Figure 1. This type of soda loss can give rise to very significant stresses that can readily cause foil fracture, Figure 2. It is interesting to note that in such foil fractures, the material behaves as a micro-composite in which the spinel layers are the hard members. Indeed, slip along the basal plane is easy but slip through the spinel blocks, at least at ambient temperature, is nearly impossible. The fracture in Figure 2 was caused by Na₂O loss from the thin foil of beta"-alumina which led to very large tensile stresses normal to the conduction planes of that part of the specimen that was being electron irradiated. The deterioration due to soda loss from beta-alumina foils seems to proceed in a somewhat different fashion, and the shear faults that lead to the formation of spinel-like intergrowths do not seem to be found in beta-alumina. The reason is that when soda is lost from sodium beta-alumina, a large number of the oxygens in the conduction plane remain, therefore preventing the collapse of the crystal. An example of a degraded beta-alumina foil is shown in Figure 3. Note that significant strain is not observed, as can be deduced from the lattice fringes that have not been displaced measurably next to the degraded region. Soda loss
during high temperature fabrication from the surface of sodium beta- and especially sodium beta"-alumina may therefore lead to significant surface stresses, and the formation of a low conductivity surface layer. Evidence of the existence of surface or near surface stresses in a sodium beta"-alumina tube may be seen in Figure 4 where bent grains were found near the surface of the tube wall but not in the center of it. We attribute the bending of the grains to high temperature deformation accommodating the stresses generated as a result of soda loss. Homogenization treatments at temperatures lower than the fabrication temperature of this material may, of course, reconstitute to some degree the surface layer. Such soda loss is not to be expected, however, as a result of electrolysis at low temperatures contrary to what has been asserted by Bovin.\textsuperscript{9} Indeed, bulk breakdown or bulk damage of beta-aluminas away from the electrode/electrolyte interfaces due to current passage was found not to occur.\textsuperscript{10} 

2) Microstructural Defects

A number of microstructural imperfections have been observed in beta-alumina: dislocations,\textsuperscript{11} complex planar faults\textsuperscript{4} or antiphase boundaries,\textsuperscript{3} 00.1 disorder and various hetero-intergrowths.\textsuperscript{12} The existence of the complex faults or the antiphase boundaries could be attributed either to profuse climb of partial glide dislocations during high temperature fabrication,\textsuperscript{4} or to an order-disorder transformation at high temperatures.\textsuperscript{3} The order-disorder transformation in beta-alumina must occur above 1500\textdegree C since the complex faults, as shown in Figure 5, decrease in density upon annealing at those temperatures. As pointed out by Le Cars et al,\textsuperscript{3} only X-ray studies near the melting point of beta-alumina could conceivably elucidate the origin of these complex faults. Another possible origin of domains may be the mode of grain growth during sintering rather than an order-disorder transformation or climb of partial glide dislocations.
When grain growth occurs, spinel ledges are nucleated on the basal planes and then propagate along them. This kind of process, described by De Jonghe, does indeed involve in the first place epitaxy of the oxygen sublattice. However, it is conceivable that the cation sublattice might be displaced with respect to that of the matrix by a partial dislocation such as the one that is terminating a complex fault or an antiphase boundary. In that way, disorder in the cation sublattice could be introduced during grain growth without the need of an order disorder transformation. It should be noted that where this complex fault or antiphase boundary intersects the conduction planes close oxygen pairs are created that are somewhat reminiscent of the close oxygen pairs that are produced when an oxygen interstitial is formed to compensate for the sodium excess. Wolf has found that the binding energy between a sodium ion and an oxygen interstitial is between 0.04 and 0.07 eV. While the close pairs that are produced by the complex fault or the antiphase boundary are not really oxygen interstitials and hence cannot act as charge compensators or affect stoichiometry of the crystal, it is still likely that some interaction exists between this kind of disturbance in the oxygen sublattice and the sodium ions. It is therefore expected that the presence of many of the complex faults or antiphase boundaries would, in fact, reduce the ionic conductivity somewhat without affecting the stoichiometry of sodium-beta alumina. No quantitative data, however, on this type of interaction are available.

00.1 disorder has been discussed by De Jonghe, Stevens, and Sato and Hirotsu. From this it follows that not all of the defects that were observed by Bevan et all could be interpreted as being beta" intergrowth into beta-alumina and, therefore, the density of planar faults and the beta" intergrowth defect is far too small to account for the sodium
excess. Rather, such planar faults are introduced during the growth of the beta-alumina crystals, and since their density is low it is unlikely that they are of much significance in the over-all conductivity of the electrolyte even though the local conductivity may be significantly affected. No significant local soda excess is expected to be associated with the planar faults, since preferential local decomposition, as observed in beta'-alumina and shown in Figure 1, did not occur.

3. Grain Boundaries

The effect of grain boundaries on the ionic conductivity of polycrystalline electrolyte has been studied by some workers and examined in some detail by De Jonghe. The most important crystallographic phenomena occurring at the grain boundaries of sodium beta-alumina is the attempt of adjacent grains to match the spinel blocks so that, as a consequence, the conduction planes can be continuous except in those places where the dislocations at the grain boundary accommodate the orientational mismatch. For all practical purposes, the spinel blocks could be treated as structureless units that attempt to be in registry. This kind of phenomenon leads to the existence of a preponderance of grain boundary dislocations with a Burgers vector \( \mathbf{b} = 1 \) spinel block. In the extreme case, complete blocking is present as shown in Figure 6. In the other extreme, almost complete continuity occurs of the conduction planes across the grain boundaries as is shown in Figure 7. There is then possible the whole range of intermediate grain boundary structures. This variety in grain boundary structures with their associated range of conductive properties will then contribute to the wide spread in relaxation times that is observed in AC measurements of the complex impedance. Clearly, grain boundaries significantly affect the ionic conductivity of a polycrystalline electrolyte. The detailed interpretation of dispersive measurements, however, seems
at present not possible since it would have to rely on the capability of constructing an absolutely equivalent electrical network of which each element has a physical significance. This difficulty clouds the interpretation that various investigators have given to the elements of simple equivalent circuits.

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References


Figure 1. Lattice image of perfect beta" (top), and faulted beta" (bottom).

The 00.3 and the 01.3 lattice fringes have been imaged. The fault in the beta" resulted from soda loss during electron irradiation in the transmission electron microscope. It is a shear type fault that has resulted from the collapse of the lattice due to removal of most of the oxygen ions in the conduction plane. The shear displacement of the spinel blocks above and below the faults removes the charge problem that would result from the double occupancy by Al$^{3+}$ of the octahedral interstices following the collapse of the oxygen bridges.
Figure 2. Foil fracture caused by soda loss to the electron microscope atmosphere during observation. The tensile stresses that result from the high shear fault density that has been produced causes both trans- and intergranular fracture. Note that the material behaves as a microcomposite in which the spinel blocks are the hard members. Since soda is not lost as a consequence of electrolysis, such degradation is not found as a consequence of cell operation.
Figure 3. Lattice image of degraded beta-alumina. The degradation resulted from the loss of soda to the electron microscope atmosphere. The soda loss in beta-alumina does not remove the majority of the oxygen ions in the conduction plane so that the crystallographic collapse and shear, as was the case in beta"-alumina, (Figure 1), does not occur. Only minor displacements of the 00.2 fringes (11.3Å) are observed, and large foil stresses leading to fracture, as was the case for beta" (Figure 2), are absent.
Figure 4. Bent grains are found near the surface of a beta"-alumina solid electrolyte tube (bottom), but not in the center of the tube (top). The bent grains are believed to be formed during sintering when stresses, generated by soda loss to the furnace atmosphere, are accommodated by climb at high temperature.
Figure 5. Complex fault network in sodium beta-alumina. The faults are predominantly on \{2\overline{1}10\} planes. These faults are cation faults in the spinel blocks, but are also anion faults in the conduction planes. The fault vector is \frac{1}{2}a<\overline{1}2\overline{1}0>. Where these faults intersect conduction planes a partial ionic blocking effect may occur. The fault density was found to decrease upon annealing around 1500°C.
Figure 6. Lattice image of a completely blocking grain boundary in sodium beta-alumina. Such blocking grain boundaries are frequently found in polycrystalline beta or beta" solid electrolytes due to the strong tendency of faceting on basal planes.
Figure 7. 6° simple tilt boundary in beta"-alumina. The tendency of the spinel blocks to match with each other is evident in this picture. An inclined edge dislocation runs from left to right through this boundary; it has a Burgers vector of 11.3 Å. Before and after the dislocation the spinel blocks are seen to attempt to match, regardless of their detailed structure.
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