

ented specimens were intermediate between those for the different draw directions. This shows that the α -relaxation arises mainly from the interior of the lamellae in specimens of nominally 80% crystallinity with little contribution from the chain folds. (A similar conclusion has been found for low-density polyethylene [6]). A similar anisotropy is observed for the γ -relaxation but this may arise to a small extent from changes in the γ_a component from oriented amorphous regions as well as from changes in the γ_c component.

Some measurements have also been made on unoriented PCTFE specimens of about 75 to 80% crystallinity after annealing for various times up to 10^5 min at 200°C in order to thicken the lamellae. Despite some inconsistencies the activation energy for the α -relaxation showed a definite trend of increasing as annealing time increased, from 2.3 to 3.0×10^5 J mol $^{-1}$, but there was no marked change in $\epsilon_s - \epsilon_\infty$. These effects are consistent with the above conclusion. The results will be used in order to test existing theory [5] assuming that this relaxation arises mainly in the interior of lamellae. The activation

energy for the γ -relaxation was little affected by annealing at this temperature.

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M. E. BAIRD
P. BLACKBURN
*Department of Applied Physics
University of Wales Institute of
Science and Technology
Cardiff, Wales*

Anisotropic electrochemical concentration cell: a system based on oriented β -alumina ($\text{NaAl}_{11}\text{O}_{17}$) as solid electrolyte

As a by-product of our interest in the electron microscopic [1] studies of layered solids and measurement of ionic migration in organic solids [2], we have been led to a brief investigation of a novel electrochemical cell in which the concentration difference occurs not in the electrolyte compartments, as is generally the case, but in the electrodes. The cell is based on β -alumina (composition close to $\text{Na}_20.11\text{Al}_2\text{O}_3$) the material now used in the high-power output, sodium-sulphur secondary battery developed at the Ford Motor Company [3-5] and elsewhere [6, 7].

The crystal structure [8, 9] of β -alumina (Fig. 1) reveals its unusual properties. The hexagonal solid has the lattice constants $a_0 = 5.58$ and $c = 22.45\text{\AA}$. Parallel to the basal plane of the hexagonal cell are sheets of atoms arranged such that four layers of oxygens are in cubic closest packing. These spinel-like blocks, within which the Al atoms occupy both octahedral and tetrahedral holes, are spaced well apart by Al-O-Al columns and within the inter-spinel spaces the Na^+ ions are arranged amongst

a set of nearly equivalent sites. The Na^+ ions are, consequently, exceptionally mobile which accounts for the very high (ionic) conductivity [6] of β -alumina.

We argued that if a single crystal of β -alumina were used as a conducting medium sandwiched between two electrodes each consisting of an inert metal immersed in an aqueous solution of Na^+ ions, then an emf could be generated, provided there is a concentration (strictly "activity") difference between the electrodes. This emf, which is proportional to the logarithm of the activities, should, however, be produced only when the crystal is oriented so as to permit ready migration of Na^+ ions along the basal planes from one electrode to the other. On turning the crystal through a right-angle, the emf should vanish because Na^+ migration is impossible along the c -direction of the solid electrolyte. This is indeed observed and the salient details of the experiment now follow.

The β -alumina used was obtained (via Mr K. Williams) from commercially available, fused, cast bricks. These bricks fracture readily, and, with care, single crystals of up to 1 cm diameter and a few mm in thickness may be extracted. The following concentration cell was set up:

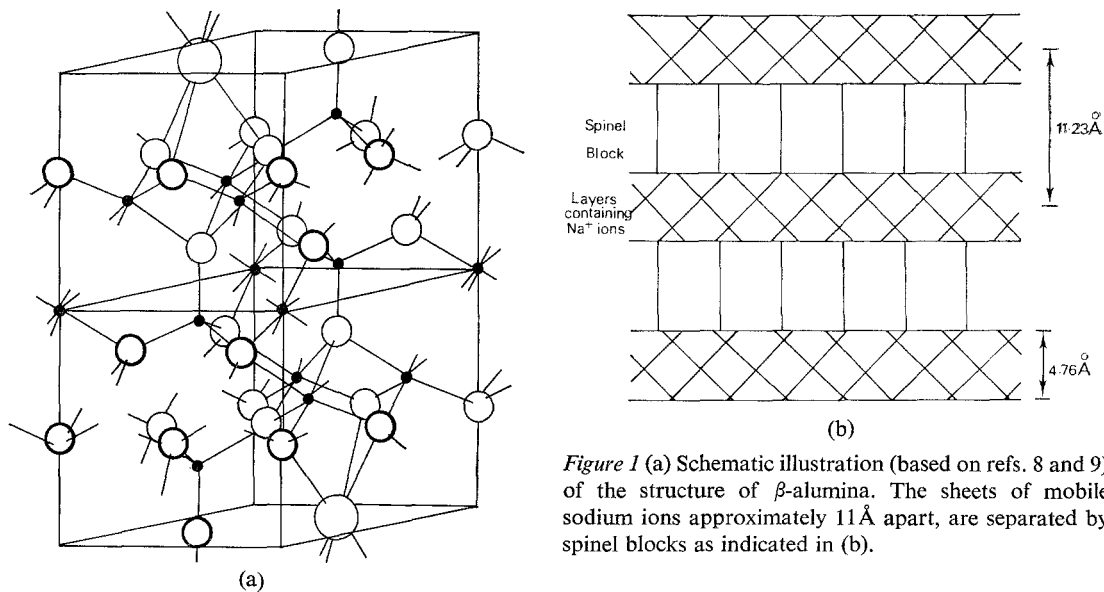
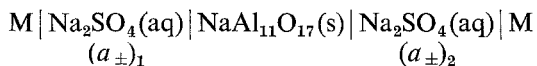


Figure 1 (a) Schematic illustration (based on refs. 8 and 9) of the structure of β -alumina. The sheets of mobile sodium ions approximately 11 \AA apart, are separated by spinel blocks as indicated in (b).



where M refers to an "inert" metal such as Pt, Ag-Cu alloy, etc. The electrode compartments were made up separately in perspex cells of capacity ~ 1.5 ml, and the crystal of β -alumina, properly oriented, used as a "bridge" for the two cells, Apiezon grease being used to hold the

solid in position. The entire assembly was mounted in a thermostat (298.0 ± 0.1 K) and measurements taken some 20 min after introducing a different solution into one or other of the compartments. Five different solutions were utilized for various combinations of the ratios of the mean activities, a_{\pm} . The actual values of the mean activities (computed from the molalities of the Na_2SO_4 solutions using the data in

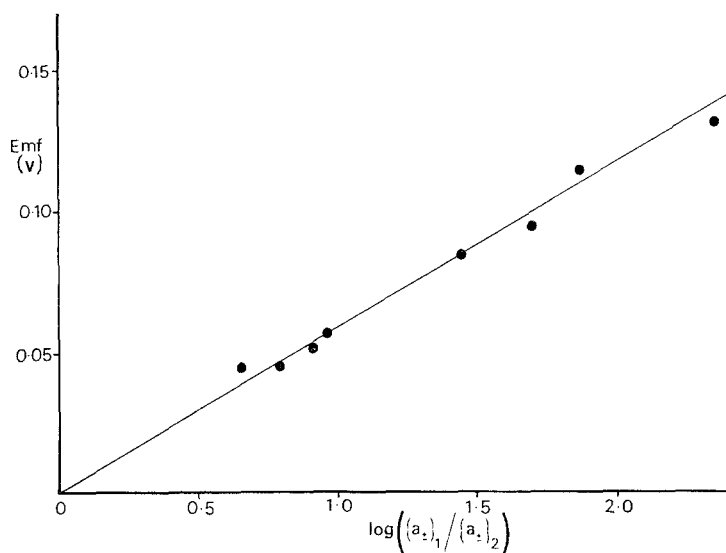


Figure 2 Plot of emf versus $\log[(a_{\pm})_1/(a_{\pm})_2]$ - see text.

Appendix 6 of ref. 10 and in Tables 4 and 5 of ref. 11) were: 0.000160, 0.00146, 0.0119, 0.0733 and 0.332. When solutions of nominally identical activities were placed in each of the electrode compartments the residual emf fell in the range 0.5 to 2.5 mV. The reading was even less (< 0.1 mV) when the β -alumina crystals were mounted with their basal planes parallel to the crystal-solution interface, even with $\log(a_{\pm})_1/(a_{\pm})_2$ ratios as large as 3.32.

Fig. 2 shows the observed dependence of emf upon the logarithm of the activity ratio at 298 K, with the β -alumina crystal in the conductivity orientation. The slope is $(0.0568 \pm 0.0025) V$ ($2.303 RT/F = 0.05916 V$ at 298 K).

A similar set of measurements carried out using various strengths of aqueous NaCl solutions (mean activities in the range 0.000102 to 0.691) as the electrodes yielded a plot similar to that shown in Fig. 2, the slope being $(0.0598 \pm 0.0070) V$.

No attempt was made to explore the pH-dependence of these concentration cells, but present work clearly indicates that β -alumina could be utilized as a form of "sodium ion-sensitive electrolyte" when the pH is close to 7. A few experiments were, however, carried out on the H_3O^+ form of β -alumina (where the sodium is replaced by hydrogen ions – prepared as described by Yao and Kummer [12]), aqueous sulphuric acid solutions (molalities from 0.0000103 to 0.0974) being used as electrodes. Again anisotropic-concentration cell behaviour was observed, though the results were rather less reproducible.

It is not irrelevant to comment that mechanically robust single crystals of highly-anisotropic solid electrolytes, used in the configurations described above, could function as useful electri-

cal switching devices in certain technological applications.

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J. M. THOMAS
A. J. WHITE
Edward Davies Chemical Labs
University College of Wales
Aberystwyth, UK

Apparatus to measure single crystal elastic constants over a wide range of temperature (RT – 1400 K)

It is desirable for many applications to know the elastic constants of materials over a wide range of temperature. This paper describes an apparatus for high temperature measurements which is relatively easy to construct. The method used to measure the elastic constants is the thin rod resonance technique [1]. In this the specimen is excited and the resonant frequencies used to

calculate the elastic constants. The arrangement is shown diagrammatically in Fig. 1. A and B are the exciting and detecting transducers. A fine untensioned wire is used to transmit vibrations to and from the specimen. All modes of vibration – longitudinal, transverse and torsional may be simultaneously excited. Depending upon the particular coupling geometry, one mode may be favoured more than the others.

The "acoustic assembly" used for measurements at room-temperature is similar to that used by other workers. It consists essentially of