suppressed as a consequence of high deformation rate, and recrystallization in this situation produces once again equiaxed grains with a random distribution of grain boundaries (Fig. 2a). The shape of the solid grain in these instances is close to Kelvin tetrakaidecahedron with the value of dihedral angle between grain boundaries being 120° when equilibrium of the forces of surface tension is established. Topological as well as thermodynamic considerations have been invoked in the study of the shapes of solid grains in annealed materials [13-15]. It has been well documented that during creep and fatigue at temperatures greater than 0.5 T_m grain-boundary sliding is an important process. When recrystallization is caused in cadmium under conditions of creep and fatigue such that grain-boundary sliding occurs, it is observed that a strong deviation from a random angular distribution of grain boundaries takes place in favour of 45° positions (Fig. 2b and c and Table I). There is clearly a determining influence of grain-boundary sliding on the process of grain-boundary migration involved in recrystallization during creep and fatigue of cadmium. This result has certainly important bearing on the observation of a tendency for the grain boundaries to align preferentially at 45° relative to the stress axis during creep and fatigue (Fig. 1b and c). A further understanding of the phenomenon seems possible only on the basis of similar topological and thermodynamic considerations as have been used in the understanding of grain shapes in annealed materials.

The authors are grateful to Professor K. P. Abraham for the provision of facilities and encouragement. One of us (PRR) acknowledges the award of a National Associateship by the UGC which facilitated a short-time visit to the Indian Institute of Science.

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Received 25 April
and accepted 4 June 1973

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Mixed conductivity of β-alumina electrolyte in aqueous concentration cells

Sodium β-alumina (Na_2O; 5.3 to 8.5 Al_2O_3 [1]) is well known for its high sodium ion conductivity, a feature which has led to its use as the electrolyte in the sodium-sulphur battery. The conductivity is highly anisotropic, being high within the basal plane of the hexagonal crystal structure, and essentially zero along the *c*-axis. This aspect was emphasized in the recent study [2] of β-Al_2O_3 single crystals as solid electrolyte in a concentration cell, where the presence or absence of an emf in the cell

$$\mathrm{Pt} \mid \mathrm{Na_2SO_4\,(aq)}_{a_1} \mid \mathrm{NaAl_{11}O_{17}\,(s)} \mid \mathrm{Na_2SO_4\,(aq)}_{a_2} \mid \mathrm{Pt}$$

was found to depend on the orientation of the crystal.

The present work was undertaken to survey the possible use of β-Al_2O_3 as a monitor for Na^+ in aqueous solutions under more general conditions.

The β-alumina was prepared in the form of a polycrystalline tube by isostatically pressing and sintering, the eventual density being greater than 3 g cm^{-3} (3.25 is a single crystal value [3]). The tube was demonstrated to be impermeable by its ability to maintain vacuum.

Platinum electrodes were applied to the tube by painting a paste (without bonding glass)* on the inside wall and sintering to 600° C for $\frac{1}{2}$ h; the outside wall electrode was a sputtered platinum deposit about 1500 Å thick. Wire connections were made to the electrodes and the whole mounted in a cell (Fig. 1) which allowed aqueous solutions of different concentrations to be passed over the two electrodes. Experiments were conducted using different Na^+ and H^+ concentrations (as NaCl and HCl). Voltages were measured on a Keithley 610 C electrometer.

TABLE I Results of concentration cell measurements

No.	Solution I	Solution II	emf at electrode II (mV)
1.	0.1 M HCl	0.01 M HCl	+ 40 ± 2
2.	0.1 M NaCl	0.01 M NaCl	+ 20 ± 2
3.	0.5 M NaCl 0.05 M HCl	0.05 M NaCl 0.5 M HCl	− 25 ± 2

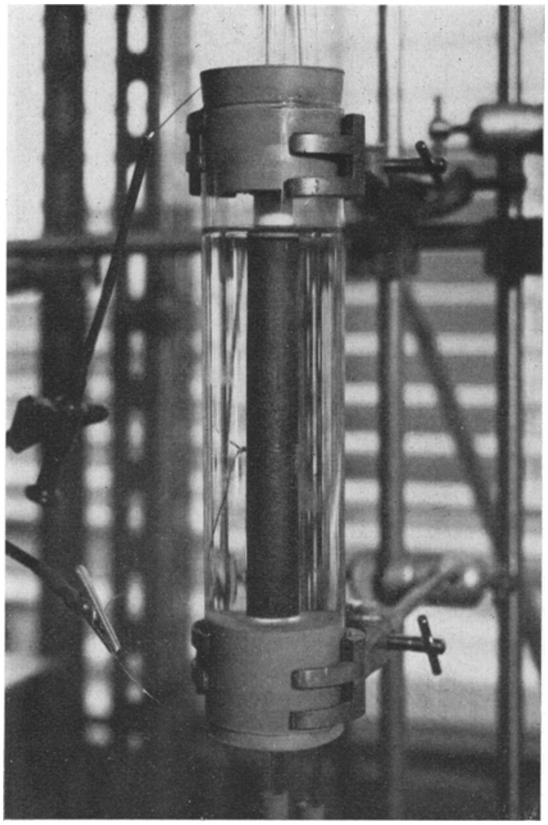

Figure 1 View of the concentration cell. One solution can be seen between the glass and the β-Al_2O_3; the second is within the β-Al_2O_3 tube.

Results for some different cell conditions are shown in Table I. These are to be compared with the expected result on the basis of an electrolyte conducting exclusively by Na^+ transport, namely

$$E = \frac{RT}{F} \ln \frac{(a_{Na^+})_1}{(a_{Na^+})_2}$$

$$\sim 60 \log \frac{[Na^+]_1}{[Na^+]_2} \quad \text{mV}$$

at 25°C assuming unit activity coefficients. On this basis, cell 2 should give values in the region of 60 mV. This was in fact found by Thomas and White in experiments [2] using single crystals and platinum electrode probes placed in the aqueous solutions but not attached to the solid electrolyte surface.

An interpretation of the present results may be made by considering the effect of a finite H^+ conductivity in the β-alumina. Under these conditions, an emf arising from a Na^+ concentration gradient can leak away by migration of H^+. Since, at steady state, the overall current is zero, and since the electronic transport number, t_e, is, by analogy with Ag-β-alumina [4], expected to be very low, the two ion fluxes are equal and opposite. Thus

$$\begin{aligned} J_{(Na^+)} &= -\, c_{(Na^+)}\, u_{(Na^+)} \left\{ \frac{d\mu_{(Na^+)}}{dx} + e \frac{d\phi}{dx} \right\} \\ &= -\, J_{(H^+)} \\ &= c_{(H^+)}\, u_{(H^+)} \left\{ \frac{d\mu_{(H^+)}}{dx} + e \frac{d\phi}{dx} \right\} \end{aligned}$$

Here c, u, $(d\mu/dx)$ and $e(d\phi/dx)$ are the concentration, absolute mobility, chemical, and electrical driving forces respectively. Putting $c_i u_i e^2 = \sigma_i$, multiplying by e^2/σ_{Total}, noting that $t_{(H^+)} + t_{(Na^+)} = 1$, and integrating from one electrode to the other, leads to the result

$$E = \left\{ t_{(Na^+)} \frac{kT}{e} \ln \frac{[Na^+]_1}{[Na^+]_2} \right\} + \left\{ t_{(H^+)} \frac{kT}{e} \ln \frac{[H^+]_1}{[H^+]_2} \right\} .$$

This expression assumes that $(d\mu/dx)$ can be written in terms of the ion concentrations in the

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*Hanovia No. 8972.

solution, i.e. that there are close to equilibrium conditions across the interface.

Applied to cell 2, the equation suggests a value for $t_{(\mathrm{Na}^+)} = 20/60 = 0.33$. The predicted voltage for cell 1, with $t_{(\mathrm{H}^+)} = 1 - 0.33 = 0.67$, is then 40 mV in good agreement with the value found (Table I). For cell 3, the predicted value is −20 mV, again in satisfactory agreement. Consequently, the results are consistent with the existence of mixed conduction by Na^+ and H^+ in the β-alumina and lead to the conclusion that, in the system used, the H^+ conductivity has a substantial role in determining the voltage present.

The reason for this observed predominance of H^+ in the determination of the emf may, by comparison with [2], arise from either the polycrystallinity of the electrolyte or the location of the platinum electrodes on the electrolyte surface. In the first case, the explanation would require an enhanced H^+ diffusion in the grain boundaries in comparison with the already high Na^+ transport in the grains. Since single crystal β-alumina has a room temperature conductivity of $0.033\ \Omega^{-1}\ \mathrm{cm}^{-1}$ [3] and since the introduction of polycrystallinity is expected to reduce the conductivity by less than a factor 10^3 [5], this explanation is perhaps unlikely in view of the observation of an internal resistance of more than $10^7\ \Omega$ in the present cells ($\sim 10^9\ \Omega^{-1}\ \mathrm{cm}^{-1}$). The second explanation is based on the platinum acting as a diffusion barrier to H^+ and to Na^+, much as was observed for oxygen diffusion in platinum electrodes on zirconia electrolytes [6]; the relative diffusivities in platinum then become more significant than those in β-alumina.

Other possible explanations, such as the existence of a high resistance surface layer resulting from $\mathrm{H_3O^+}$ or neutral water penetration into the lattice [3], or the existence of low exchange rates at the Pt electrode probes, are not consistent with the observed differences between the present work and that of Thomas and White [2].

Two conclusions may, therefore, be drawn from the programme. First, it is clear that the use of β-alumina as a monitor in aqueous solutions is unlikely to be practicable since the emf is influenced not only by the Na^+ but also by the presence of those other ions that can move in the lattice Ag^+, Li^+, K^+, Tl^+, Rb^+ and perhaps others [3]; the relative importance of these will in turn be influenced by the structure and location of the metal probe electrode. The second item is that the results show migration of H^+ (or perhaps less likely of $\mathrm{H_3O^+}$) in Na-β-alumina, and that this species too must accordingly be included in the above list.

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Received 24 April
and accepted 6 June 1973

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