## *Thermal stability of hyarogen-exchanged β-alumina*

Replacement of the cations in sodium β-alumina by hydrogen ions has been known for some time [1, 2]. However, the mobility of these ions has only recently attracted interest. This has been stimulated in part by the realization of the potential usefulness of hydrogen ion conductors for a variety of applications, reinforced by the fact that solid materials exhibiting this property are rare [3]. In a study of mixed conductivity of β-alumina electrolytes in aqueous concentration cells [4], speculation began on the precise form in which mobile hydrogen ions were incorporated in the structure (namely $H^+$ or $H_3O^+$ ions). It continued with subsequent hydrogen gas monitoring experiments [5]. In the present letter we extend this work by studying the effect of moisture on the response of sodium β-alumina to hydrogen activity changes, and also the thermal stability of fully hydrogen-exchanged materials.

Fig. 1 shows the way in which the 1 mm thick partially hydrogen-exchanged β-alumina sensing element was mounted in a Kodial glass envelope [6]. Contacts were made using platinum paste fired to 600° C, platinum leads being would round the outside and sprung against the inside of the elements. This arrangement gives reasonable service, but the difference in thermal expansion between glass and tube, and especially the change in lattice parameter of the tube during exchange, eventually causes failure. Kodial glass was chosen because it provides the closest expansion match of the easily worked glasses. The output voltage of such a cell was measured conventionally. Commercial $H_2/N_2$ was dried when appropriate using Molecular Sieve 5A, which gives a water vapour content $<0.06$ p.p.m. by volume [7]. Gas of fixed compostion was directed onto the reference electrode of the sensing element, whilst the partial pressure of hydrogen incident on the sense electrode was altered step-wise by a factor of 2 using a Digital 101 gas mixer [8], the diluent being nitrogen.

Fully hydrogen-exchanged β-alumina was prepared by first exchanging the sodium for silver in polycrystalline samples by immersion in a large molar excess of molten silver nitrate at 220° C for 24 h. The reaction is:

$$AgNO_3 + Na_2O \cdot xAl_2O_3 \rightarrow Ag_2O \cdot xAl_2O_3 + NaNO_3 \cdot$$

The weight change of the sample allowed the factor $x$ to be determined as approximately 8.9.

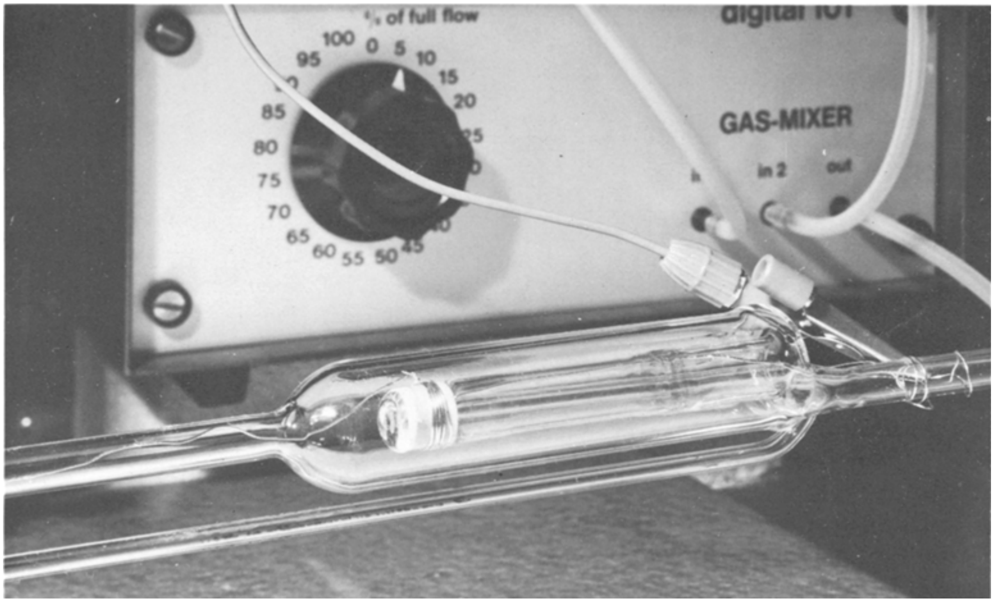

*Figure 1* β-alumina tube sealed to Kodial glass for gas monitoring experiments. Reference gas flows through the larger tube on the left, past the outer β-alumina surface and out via the tube on the right. The smaller tube in the foreground is U shaped and directs the gas of variable composition (mixed in the digital gas mixer shown in the rear) at the inner surface of the specimen. Platinum leads contact part of the specimen sputtered with the same metal.

Following removal of excess nitrate, the material was reduced using dry hydrogen gas at 350° C. During this process the artefact (usually a section of tube) crumbles, owing to the diffusion of silver into the grain boundaries and the increase in lattice parameter. On exposure to the air, the hydrogen $\beta$-alumina increases rapidly in weight, indicating uptake of moisture:

$$Ag_2O\,8.9Al_2O_3 + H_2 \rightarrow H_2O \cdot 8.9Al_2O_3 + Ag$$

(hydrogen $\beta$-alumina)

and then

$$H_2O \cdot 8.9Al_2O_3 + 2H_2O \rightarrow (H_3O)_2O \cdot 8.9Al_2O_3$$

(hydroxonium $\beta$-alumina)

This second process is enhanced by boiling the resulting hydroxonium $\beta$-alumina/silver mixture in hot nitric acid until all the silver has been removed. X-ray powder diffraction indicates the presence of only $\beta$-alumina phases at the end of this procedure.

The results obtained for moist and dry gas monitoring using a $Na\beta$–$Al_2O_3$ sensor at room temperature are shown in Fig. 2. The form of the results is explained as follows. When the hydrogen partial pressure at the sense electrode is $P_1$ the cell voltage is given by the Nernst equation:

$$V_1 = -(RT/nF)\ln(P_1/P_{\text{ref}}) \qquad (1)$$

where $R$, $T$ and $F$ have their usual meaning, and $n$ is the number of electrons per molecule of reactant in the half cell reaction. On changing $P_1$ to $P_2$ we have:

$$V_2 = -(RT/nF)\ln(P_2/P_{\text{ref}})$$

Hence

$$\Delta V = V_1 - V_2 = -(RT/nF)\ln(P_1/P_2) \qquad (2)$$

The Digital 101 gas mixer allows us to make $P_1/P_2$ either $\frac{1}{2}$ or 2 (for convenience). Besides being dependent on $P_1/P_2$, the sign of the voltage also depends on the sign of the charge carrier in the electrolyte. The results show that the charge carrier in the electrolyte is positive (provided it is a hydrogen ion), and that in Equation 1, $n = 2$ ($\Delta V$ (average) $= 8.5$ mV). The proposed half cell reaction is:

$$H_2 \rightarrow 2H^+ + 2e$$

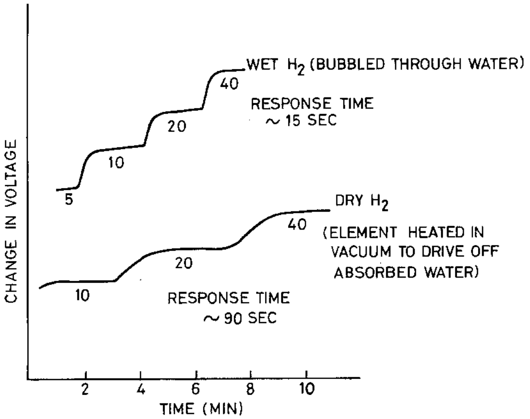

*Figure 2* The difference in response of the $\beta$-alumina element to wet and dry hydrogen gas.

with the possible complication of:

$$H^+ + H_2O \rightarrow H_3O^+$$

since the gas was moist. Current in the electrolyte is carried by either $H^+$ or $H_3O^+$, a result which correlates with that found in the aqueous monitoring experiments.

Fig. 2 also shows the difference in response at room temperature when the gas is as dry as can conveniently be achieved in the laboratory. Essentially, the voltage change is the same, but the response time is increased from about 15 sec to approximately 90 sec. Two extreme explanations are available for this change. Either the same ion is mobile in the electrolyte, but the presence of moisture has no catalytic effect but reacts with $H^+$ at the electrode, producing $H_3O^+$ in the electrolyte. This latter possibility is reinforced by the observation that $H_3O^+$ is apparently more mobile in $\beta$-alumina than $H^+$ [10] and more mobile carriers will clearly give a faster response. The true explanation possibly lies between these extremes, but it does appear that different carriers may be present in the electrolyte when wet and dry gas are used.

This difference in response suggested the need to prepare fully hydrogen-exchanged material. Its thermal stability was investigaged using DTA and DTG, and by X-ray powder diffraction. Fig. 3 shows the former results. The outstanding features of the DTG trace are the two regions of weight loss between 75 and 380° C, and 650 and 885° C. From the TG trace the percentage weight loss in these temperature ranges was 3.0 ± 0.5% and

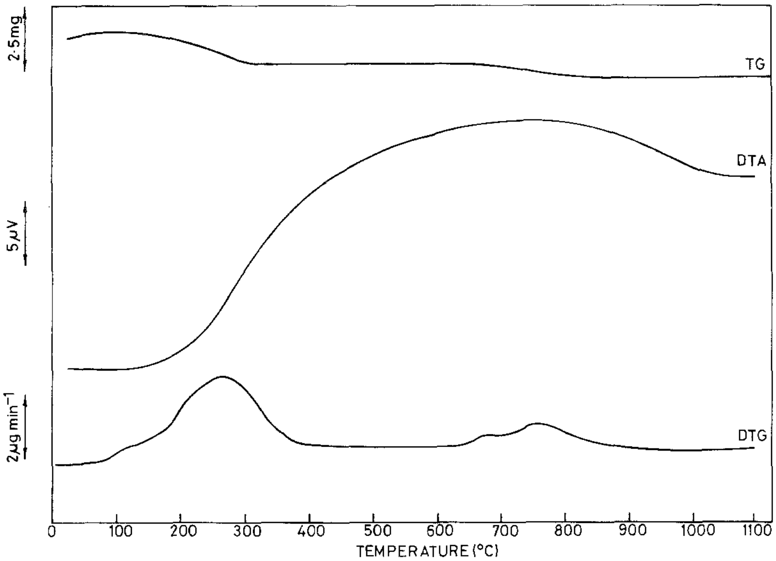

*Figure 3* DTA, DTG and TGA traces for the decomposition of fully hydrogen exchanged β-alumina.

1.1 ± 0.5% respectively. Coincident with the start of the first DTG peak is the leading edge of a broad exothermic peak which continues almost up to the maximum temperature of 1100° C, when it shows signs of levelling off. The most likely two-step decomposition of hydroxonium β-alumina is:

$$(H_3O)_2O \cdot 8.9Al_2O_3 \xrightarrow[75 \text{ to } 380^\circ \text{C}]{-2H_2O} H_2O \cdot 8.9Al_2O_3$$

$$\xrightarrow[650 \text{ to } 885^\circ \text{C}]{-H_2O} 8.9Al_2O_3$$

from which we can calculate theoretical weight losses of 3.7% and 1.8% respectively. Within experimental limits the above decomposition scheme fits the observed weight losses, particularly if one recognises that the stoichiometry of the material is difficult to determine. Following the thermogravimetric runs an X-ray diffraction pattern of the sample showed only diffuse lines, indicating that if any β-alumina is present, it is microcrystalline or amorphous.

The X-ray diffraction study of the thermal decomposition of the fully exchanged material was performed by heating powder samples overnight in air at a variety of temperatures and then taking room temperature X-ray diffraction patterns. As shown in Fig. 4, up to 500° C the pattern remained essentially unchanged, showing that the β-alumina structure exists through the first stage of decomposition. After 12h at 700° C or 1 h at 800° C the high angle β-alumina lines, but not the low angle lines, become diffuse, and there are no α-alumina lines present. After the 950° C anneal all but the two lowest angle β-alumina lines remain, but much more indistinct than previously, and the α-alumina lines become sharp. Treatment at 1300° C causes the disapearance of all β-alumina lines, with only α-alumina lines present, showing full transformation to this phase. These results affirm the decomposition model proposed above, and also provide a useful means of assessing the degree of exchange of a sample which was previously Naβ–$Al_2O_3$. By heating the sample to 1300° C, all the hydrogen-exchanged material is transformed to α-alumina whilst the unexchanged β-alumina phases give their usual distinct pattern. Below ~250° C hydrogen β-alumina can be found in either $H^+$ or $H_3O^+$ forms depending on its history and present environment, but above this temperature, only $H^+$ β-alumina is stable. This confirms inferences which may be drawn from work published elsewhere [9].

In summary, partially hydrogen exchanged sodium β-alumina has been shown to act as an element sensitive to hydrogen activity, but with response dependent on the moisture content of the gas: it is much more rapid for moist gas. At near ambient temperature the more mobile ion appears to be the hydroxonium ion, whilst at high temperatures only the hydrogen ion containing material is stable, and the conductivity appears to be reduced as a result. Fully hydrogen exchanged

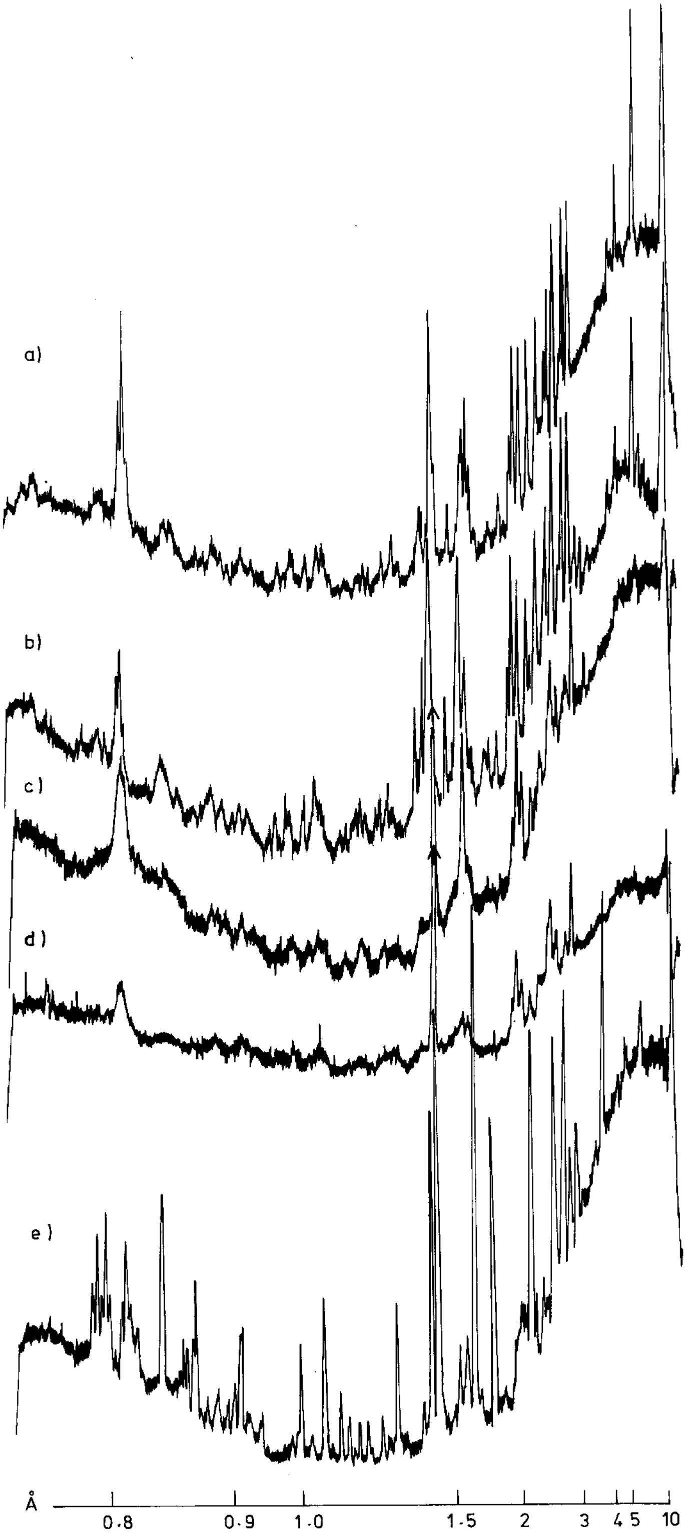

*Figure 4* Room temperature X-ray powder diffraction patterns taken on samples of hydrogen β-alumina annealed at (a) 100° C for 15 h, (b) 500° C for 15 h, (c) 700° C for 15 h, (d) 800° C for 15 h, (e) 1100° C for 15 h.

β-alumina has been shown to decompose by a two-step process. The final temperature of structural breakdown is much higher than is usually found for other compounds containing hydrogen.

## Acknowledgements

We should like to thank Dr G. J. May, Chloride Silent Power Ltd., and Mr R. J. Bones, AERE Harwell for provision of the β-alumina used in this work, Professor R. J. Brook and Dr A. E. Hughes for valuable discussions, and Mr K. T. Harrison for taking some of the X-ray powder diffraction patterns. Mr D. Gilling also helped collect the experimental data.

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*Received 22 June*
*and accepted 25 July 1977.*

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## *Estimation of quartz in silica bricks by infrared spectra*

The need to know α-quartz content in a fired silica brick (principally consisting of tridymite and cristobalite) used as a refractory material, arises because the expansion and contraction phenomena associated with this phase during transformation leads to cracking and spalling of the bricks while in use. Difficulties have been experienced in detecting unambiguously α-quartz present in low percentages by X-ray diffraction because of the overlapping of the tridymite XRD line with that of the most intense line of α-quartz at 3.34 Å.

The infrared spectral method has been found useful below 900 cm$^{-1}$ as a complimentary method to estimate the quartz concentration in silica bricks. This is possible because of the characteristic peaks of the phases in this region. α-quartz has a sharp band at 690 cm$^{-1}$ while cristobalite has a similar band at 620 cm$^{-1}$. Tridymite has no such band however. The other bands of these phases are overlapping (Fig. 1, Table I).

A routine potassium bromide pellet technique using the standard setting of the i.r. instrument (Perkin Elmer 621) was adopted as reported earlier in connection with an estimation of dolomite mineral [1]. The only difference in the sampling technique was to increase the amount of the sample in the KBr pellet (about 5 to 6 mg in 250 mg of KBr) so that an appreciable intensity of the 690 cm$^{-1}$ band was obtained. The presence of quartz as low as 2% in the sample can thus be detected in the brick. The intensity of the 690 cm$^{-1}$ quartz band varies in the spectra of brick samples, with 12% quartz (brick No. 1),

TABLE I Infrared data of silica polymorphs in the 900 to 400 cm$^{-1}$ region

| α-quartz | Tridymite | Cristobalite | Brick sample No. 1 | Brick sample No. 5 |
|---|---|---|---|---|
| 790 sh | | | | |
| | 780 | 785 | 787 s | 786 |
| 775 | | | | |
| | | | 691 w | |
| 690 sharp | | | | |
| | | 620 sharp | 620 | 620 |
| 510 sh, br | | | | |
| | | 470 s, br | 470 | 473 |
| 460 br | 460 s, br | | | |

br = broad, s = strong, sh = shoulder, w = weak