The use of β-alumina electrolyte in gaseous concentration cells

In an earlier note [1], the use of β-alumina [2] electrolyte as a membrane in an aqueous concentration cell was described; although the cell was found to behave in a predictable manner, the fact that the electrolyte showed mixed conduction by alkali ions and by hydrogen ions greatly restricted its use as a monitor for the concentration of a particular ion type.

More recently, Choudhury [3] has demonstrated the ability of two-phase α-alumina/β-alumina mixtures to act as monitors for oxygen and aluminium activities at temperatures above 550° C, the requirement for two phases being that a fixed oxygen or aluminium activity should then define the system thermodynamically.

In the present note, the use of β-alumina in ambient temperature gaseous concentration cells is described. The material employed is, as before, a mixed β/β″ alumina of density greater than 3 g cm^{-3}. The sensing element was prepared from a polycrystalline tube by cutting off a 1 cm length and by machining the inner and outer surfaces down to a wall thickness of 1 mm.

Platinum electrodes were prepared to a thickness of about 1500 Å on both surfaces by sputtering, and the element was mounted in a cell (Fig. 1) which exposed the two surfaces to different gas streams. The feed gases used were H_2, H_2–N_2, O_2, and O_2–N_2, the mixed gases being prepared in a digital gas mixer [4] (Digital 101); all gases were saturated with water at 23° C.

The element was tested as monitor for hydrogen and for oxygen. In each case the test consisted of exposing the element to the pure gas and to mixtures of the pure gas with nitrogen; the emf of the cell was then followed as the dilution of the pure gas in the nitrogen mixture was changed.

Results for hydrogen are shown in Fig. 2, where it can be seen that changes in dilution of a factor of two resulted in variations of emf averaging 8.5 mV. This is in accord with the expected voltage change for migration of charge carriers in the β-alumina with conventional charge, that is as H^+ or H_3O^+. Then the Nernst equation gives

$$E = \frac{RT}{2F} \log_e 2$$

which for ambient conditions is 8.8 mV. The absolute value of the emf shows an offset from the theoretical value, indicating that at this temperature, the element is acting under quasi equilibrium, as is expected from the fact that time needed for electrolyte equilibration [3] is much in excess of the response time shown in Fig. 2. The use of a single phase system would also preclude the occurrence of stable absolute emfs (the finding that β″ is a metastable form [5] of β indicates that the β″/β mixture cannot be treated as a two phase system) because the overall system is then incompletely defined thermodynamically.

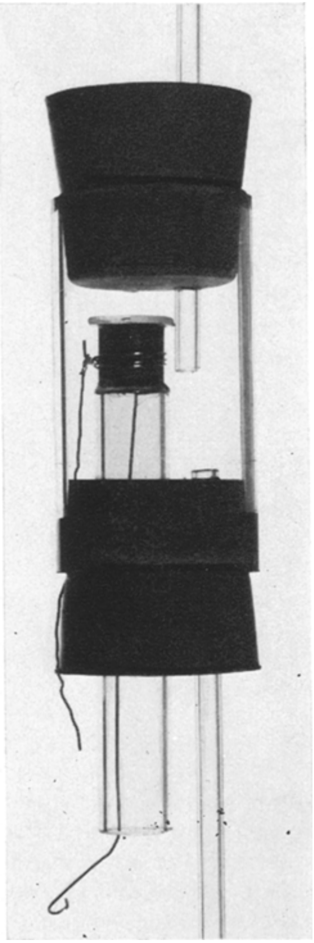

Figure 1 View of the gaseous concentration cell.

Results for the monitoring of oxygen activity are given in Fig. 3. Two factors may be noted: first that the response time is considerably slower and secondly that the emf change of 18 mV is four times greater than that predicted for

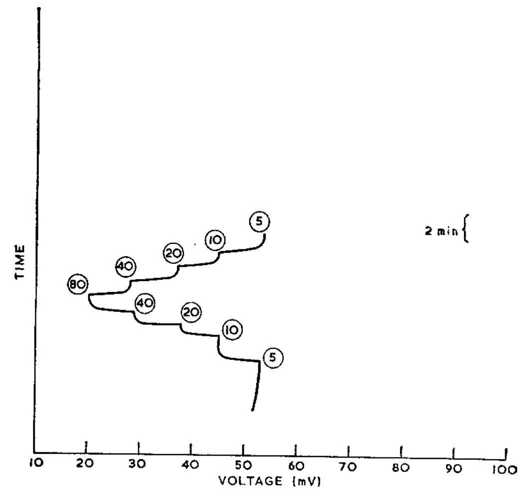

Figure 2 β-alumina as a hydrogen monitor; the percentage of hydrogen in the mixed gas (balance nitrogen) is indicated, the reference gas being pure hydrogen in all cases.

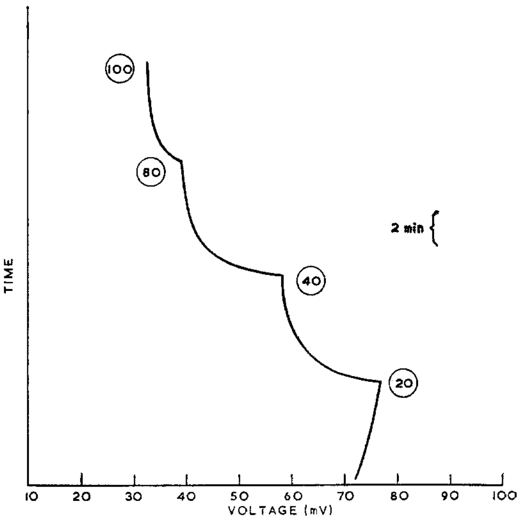

Figure 3 β-alumina as an oxygen monitor; the percentage of oxygen in the mixed gas (balance nitrogen) is indicated, the reference gas being pure oxygen in all cases.

migration of conventionally charged species, as, for example, O^{2-},

$$E = \frac{RT}{4F} \log_e 2 \sim 4.4\text{mV}\,.$$

The explanation for this second effect can take a number of forms. It may be that a carrier such as O_2^- is responsible for oxygen transport, in which case the predicted emf is then as found. On this basis experiments were made to detect O_2^- by observing fluorescence excited by a mercury arc and by a He/Cd laser at 300 and 77 K; fluorescence attributable to O_2^- was not found. The emf value would also be explained by electrode reactions of the type [6]

$$2O_2(g) + 2e^- \rightarrow O^{2-} + O_3$$

where the resulting O_3 is taken to reach a stable saturation value at the electrode. A third possibility is that the signal represents a mixture of a quasi equilibrium condition with a slower background drift toward true equilibrium; for reasons noted above in respect to hydrogen, and from the form of Fig. 3, this last explanation would appear unlikely.

In summary, the element can be used in the presence of moisture as a fairly rapid response monitor for changes in hydrogen activity; for oxygen, the ambiguity of interpretation and the slower response time make the element less satisfactory.

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