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$Ca_{12}Al_{14}O_{33}$ – A possible high-temperature moisture sensor

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$C_{12}Al_{14}O_{33}$ is a high temperature oxide ion conductor whose conductivity is very sensitive to the presence of water vapour for temperatures in the range ∼ 1000 to 1200° C. The changes are reversible and the conductivity may be recovered by heating in a dry atmosphere. Applications in an amperometric device are envisaged.

1. Introduction

We have recently found [1, 2] that $Ca_{12}Al_{14}O_{33}$ is an oxide ion conductor at high temperatures, whose conductivity is only 8 to 10 times lower than that of yttria-stabilised zirconia. As such, it could have applications in oxygen sensors and in fuel cells. It has the additional advantages of being easy to prepare and fabricate into ceramic pellets; by careful attention to the firing conditions, the magnitude of the grain boundary resistance can be reduced to the extent that the total pellet resistance is dominated by the intrinsic resistance of the grains [3].

$Ca_{12}Al_{14}O_{33}$ has an unusual crystal structure with two types of anion: a three dimensional aluminate framework constructed of corner-sharing tetrahedra, of stoichiometry $[Al_{14}O_{32}]^{22-}$ and one additional oxide ion per formula unit [4]. This additional oxide ion can be replaced by various other anions, including halide, superoxide and hydroxide [5–8], although the precise stoichiometry of some of these materials is not clear. Thermogravimetric studies [8] indicated that $Ca_{12}Al_{14}O_{33}$ reacts with water at temperatures above about 900° C, as shown by a gradual increase in weight and it was suggested that this was due to the reaction:

$$Ca_{12}[Al_{14}O_{32}]O + H_2O \longrightarrow Ca_{12}[Al_{14}O_{32}](OH)_2 \qquad (1)$$

Here we report measurements of the conductivity after treatment in various atmospheres which both confirm the sensitivity to water vapour and suggest a possible application as a moisture sensor.

2. Experimental details

Details of the preparation of ceramic samples of $Ca_{12}Al_{14}O_{33}$ were given previously [1, 2], together with information on the fabrication of platinum electrodes, the conductivity jig and the ac impedance instrumentation, based on the Solartron 1250/1286 frequency response analyser and electrochemical interface. During the present measurements, samples were exposed to various atmospheres and the changes in conductivity monitored.

3. Results

A pellet of $Ca_{12}Al_{14}O_{33}$ was used that had been heated at ∼ 1350° C so as to give a well-sintered sample with small grain boundary impedances. The impedance data were analysed as described previously [1, 2], by plotting them in the complex impedance plane and values of the bulk, intragranular resistance extracted from the appropriate intercept of the data on the real, Z' axis.

Fig. 1 shows bulk conductivities measured over the temperature range 300 to 1100° C for the sample after exposure to laboratory air at different temperatures for 16 hours. Results 1 are for the fresh pellet sintered at 1363° C. Results 2 are for the same pellet after heating at 910° C. It can be seen that the conductivity has decreased by half to one order of magnitude, depending on temperature. On reheating at 1255, 1300 and 1335° C, the conductivity gradually recovers as seen in data sets 3 to 5. On reheating at 1000° C, set 6, the conductivity decreases again and then fully recovers its original value on heating at 1349° C, set 7. When the same sample was heated at temperatures of 700° C or lower, no changes in bulk conductivity could be detected.

The conclusions to be drawn from these experiments is that the sample is atmosphere sensitive over the approximate temperature range 900–1300° C but that the conductivity can be recovered by heating at higher temperatures. The degree of recovery depends on temperature. Complete recovery occurs only when the sample is heated close to the original sintering temperature. This temperature is close to the melting point of $Ca_{12}Al_{14}O_{33}$, variously quoted as being in the range 1360 to 1390° C [9].

Experiments were then carried out at a constant temperature of 1170° C and the conductivity monitored as a function of atmosphere. The results, Figs 2 and 3, showed conclusively that moisture was responsible for the changes in conductivity. Thus, in Fig. 2 are shown the results of cycling between lab. air, dry air (bubbled

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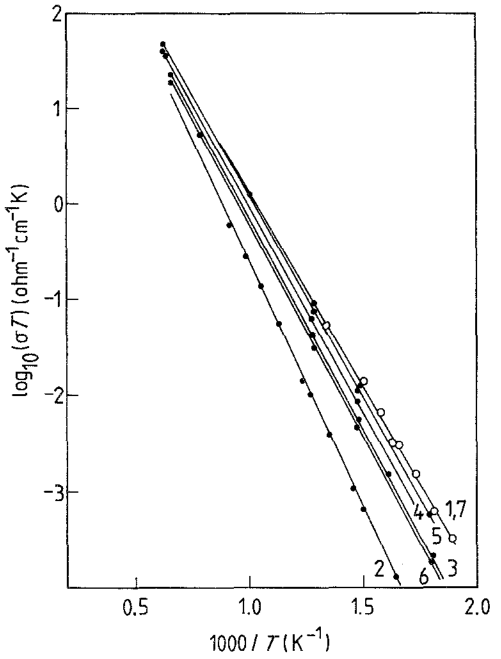

Fig. 1. Bulk conductivity of $Ca_{12}Al_{14}O_{33}$ after sequentially annealing, for 16 hour periods in lab. air, at the following temperatures (° C): 1, 1363; 2, 910; 3, 1255; 4, 1300; 5, 1335; 6, 1000; 7, 1349.

through conc. H_2SO_4), wet air (bubbled through water) and vacuum. The conductivity decrease observed in lab. air is magnified in wet air but the conductivity is recovered either in dry air or in vacuum. Clearly, the partial pressure of water is a critical parameter at this temperature. In Fig. 3 are shown results for the sample cycled between wet nitrogen and dry CO_2. The results are similar to those of Fig. 2 and demonstrate conclusively that H_2O and not CO_2 is responsible for the conductivity changes.

It was shown earlier [2] that, in dried samples, the transport number of oxide ions is essentially unity. These experiments were repeated for samples that had been exposed to moisture, with the conclusion that oxide ions were still the predominant conducting species. Details are as follows.

A dried pellet with bulk conductance at 990° C of 1.08×10^{-4} ohm^{-1}, was placed in a concentration cell [2] at 990° C and the two pellet surfaces exposed to moist atmospheres with a partial pressure ratio for H_2O of 4 : 1. This was achieved by passing the air through water bubblers at 29 and 7° C, respectively. The emf generated by such a cell was 0.0 ± 0.1 mV, compared with the value of 77 mV expected if the conduction were due entirely to hydroxide ions. This showed the transport number of hydroxide ions to be no greater than 0.001, consistent with previous results [2].

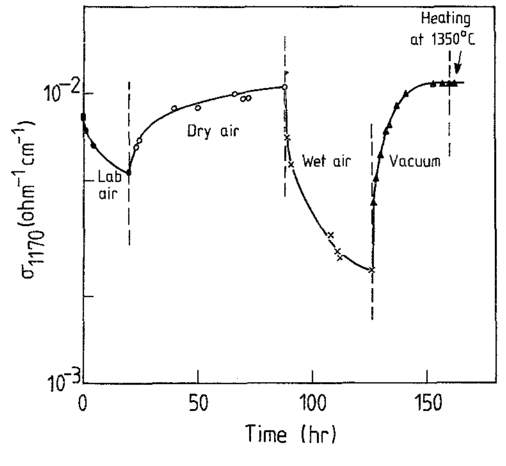

Fig. 2. Ionic conductivity of $Ca_{12}Al_{14}O_{33}$ at 1170° C as a function of time in different atmospheres.

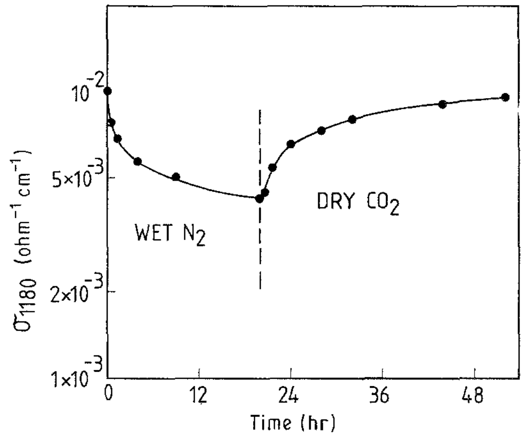

Fig. 3. Ionic conductivity of $Ca_{12}Al_{14}O_{33}$ at 1180° C as a function of time in two different atmospheres.

The experiment was then repeated after the sample had been exposed to wet air at 990° C for 16 hours and its conductance had decreased to 2.7×10^{-5} ohm^{-1}. The measured emf was now 2.1 ± 0.1 mV, indicating a non-zero transport number for hydroxide ions of 0.027. The majority carriers were still oxide ions as shown by changing the atmospheres in the concentration cell to air and oxygen; accurate measurements were not made but the voltage rose rapidly to at least 22 mV, which was about 60% of the theoretical value of 38 mV. Thus, oxide ions are the predominant carriers but, on increased exposure to moisture, the transport number of hydroxide ions may increase. It would be interesting to measure the transport number at slightly lower temperature on samples subjected to a prolonged exposure to moisture in order to determine the optimum transport number for hydroxide ions.

The results on the sensitivity of the sample to moisture, Figs 1 to 3, do not necessarily represent the equilibrium conditions at each temperature; further work is required to ascertain the equilibrium behaviour and to study the time dependence of moisture pick-up and loss. It is interesting that the thermogravimetry results [8] indicated that, at 990° C, ~ 95% of the extra oxide ions were converted to hydroxide ions; this is also consistent, qualitatively, with the decrease in conductivity being due to the decrease in number of mobile or available free oxide ions. An additional uncertainty which must be clarified before a quantitative understanding is obtained concerns the possible presence of superoxide ions in place of oxide ions. These have been reported to be present [7], but the conditions for their introduction/removal have not been established.

4. Conclusions

$Ca_{12}Al_{14}O_{33}$ is an oxide ion conductor whose conductivity is sensitive to moisture over the range ~900–1300° C. Possible use could be made of this in amperometric devices.

Acknowledgement

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