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Zirconia electrolyte cells

Part 2 *Electrical properties*

K. C. RADFORD, R. J. BRATTON
Westinghouse Research and Development Center, Pittsburgh, Pa 15235, USA

The electrical conductivity of zirconia electrolyte cells containing Al_2O_3 and TiO_2 sintering aids made by conventional cold pressing and sintering procedures, and also by the tape process with co-fired electrodes, are compared with the conductivities of undoped material.

1. Introduction

Zirconia electrolyte cells can be made economically and with reproducible properties by using the tape process [1], the technique most often associated with alumina substrate manufacture in the electronics industry. One of the main advantages of this type of manufacture is that the electrode material, generally Pt, can be applied to the green ceramic tape by spraying or screen printing prior to sintering. On sintering, the electrolyte densifies into an impervious body while the electrode becomes intimately bonded, forming a conductive, porous coating that requires no additional processing. This is in contrast to normal procedures which require several sintering operations to provide a Pt layer having sufficient electrical conductivity. The only limitation to the process is that the sintering temperature of both the ceramic electrolyte and the Pt electrode must be below about 1500° C to avoid the rapid evaporation of the Pt which occurs at higher temperatures. While zirconia powders having high sinterability are available, a substantial cost incentive results by using grades of zirconia which are less reactive and which are normally sintered at temperatures in excess of 1700° C but which can be prepared at lower temperatures by using sintering aids.

In a previous paper [2] it was shown that several grades of zirconia could be sintered both in pellet and tape-produced form at 1480° C using Al_2O_3 and TiO_2 additions. This paper reports the electrical properties of the tape derived material and compares its behaviour with that of conventionally cold pressed and sintered material both with and without the additives.

2. Experimental procedures

Tapes of technical grade 5 wt% CaO stabilized ZrO_2 (CSZ) containing 2 mol% Al_2O_3 and 5 mol% TiO_2 were prepared as reported previously [2] having thicknesses of about 0.050 in. Before sintering, Pt electrode materials were screen printed onto both surfaces to a thickness of about 0.004 to 0.006 in. The metallization composition was prepared in a similar manner to the tapes; –325 mesh Pt powder was mixed with 1% deflocculating agent*, 2% polyvinyl butyral† binder and 10% fine-grained zirconia powder‡ in butyl carbitol acetate solvent. The tapes were sintered in air at 1480° C for 3 h giving densities of 93 to 95% theoretical density (TD), and the thickness shrinking to about 0.025 in. with a metallization thickness of about 0.002 in.

Electrical conductivity data were also obtained on cold pressed and sintered pellets of CSZ of both technical and nuclear purity§. These pellets were sintered at 1690° C to give densities approximately 93% TD. Also, pellets containing 5 mol% TiO_2 and 1 mol% TiO_2, sintered at 1480° C for 3 h were evaluated. Pt electrodes were applied to

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*ENSIGN Z3 (air treated) Jesse S. Young Co., New York, NY, USA.
†Type B76, Monsanto Corp., St. Louis, MO, USA.
‡$(Y_2O_3)_{0.09}(ZrO_2)_{0.91}$ obtained from W. R. Grace, Co., Clarksville, MD, USA. Average particle size ~ 1 μm.
§Technical grade purity nominally 97%; Nuclear grade nominally 99.7%.

the pellets by repeatedly coating the two surfaces with a thin layer of the Pt slurry and sintering at 1200° C in air until a conductive, porous layer was obtained.

The electrical conductivities were measured using a Wayne–Kerr Universal Bridge #B221 at frequencies from 10 000 to 20 000 Hz using a signal generator #S121. Conductivity measurements were made up to 1000° C in air using a vertical Pt-wound resistance furnace, and the temperature measured with a chromel–alumel thermocouple. Temperature control was maintained by a proportional controller and a saturable core reactor power supply to provide stability to ±2° C. Equilibration of the sample at each temperature was ensured by repeated conductivity measurements over a period of days. The sample was supported in the centre of the furnace on an alumina tube pedestal and kept in position by a spring-loaded alumina tube on top. Contact was made to the samples with Pt discs and lead wires. The data were least-squares fitted to a linear $\sigma - 1/T$ dependence.

3. Results

The adhesion of the metallization to the tapes was found to be excellent. The metallization could not be removed except by severe abrasion. Metallographic sections of metallized tapes containing Al_2O_3 and TiO_2 are shown in Fig. 1, which clearly reveal the intimate bonding between the ZrO_2 in the tape and in the metallization since no identifiable interface can be seen and the Pt particles are effectively locked in place.

Electrical measurements showed that pressed and sintered pellets of both technical and nuclear grades of CSZ gave essentially the same conductivities, exhibiting a linear log $\sigma - 1/T$ relationship. The doped material showed an anomalous behaviour in that during the testing at 1000° C the conductivity slowly declined over the period of two or three weeks before stabilizing at a value approximately ten times lower than that of the undoped material. The conductivities of the pellets containing 5 mol% TiO_2 and 1 mol% Al_2O_3 were very similar. Conductivity plots are shown in Fig. 2, and the activation energies and pre-exponential factors listed in Table I.

TABLE I Conductivity data for CSZ (conductivity, $\sigma = A^{-Q/RT}$)

Material	Pre-exponential term, A	Activation energy, Q (cal)
Pressed pellets		
1 Nuclear purity	1244	25 060
2 Technical purity	2364	26 650
3 + 5 mol% TiO_2	2229	31 100
4 + 1 mol% Al_2O_3	211	25 680
Tapes		
5 + 2 mol% Al_2O_3	1200	28 625
6 + 5 mol% TiO_2	670	31 630

The tape material also exhibited this initial drift in conductivity before stabilization. The Al_2O_3-bearing tape showed a slightly higher conductivity than the pressed pellets containing TiO_2 and Al_2O_3, whereas the TiO_2-bearing tape exhibited a lower conductivity. The activation energies of the TiO_2-doped tape and pellet materials were very similar, and were somewhat larger than those for the undoped material. The activation energy increased with Al_2O_3 content.

4. Discussion

The ability to sinter zirconia electrolytes with co-

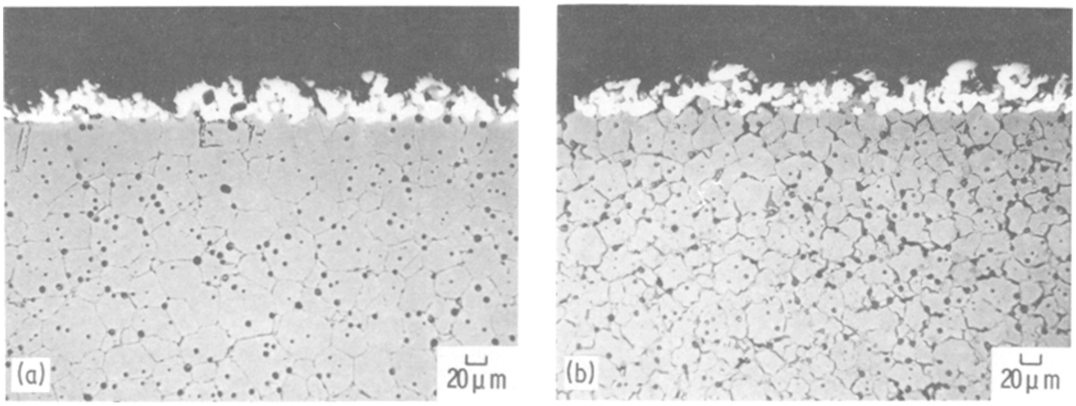

Figure 1 Etched microstructure of CSZ showing co-fired Pt electrodes (a) with 5 mol% TiO_2, (b) with 2 mol% Al_2O_3.

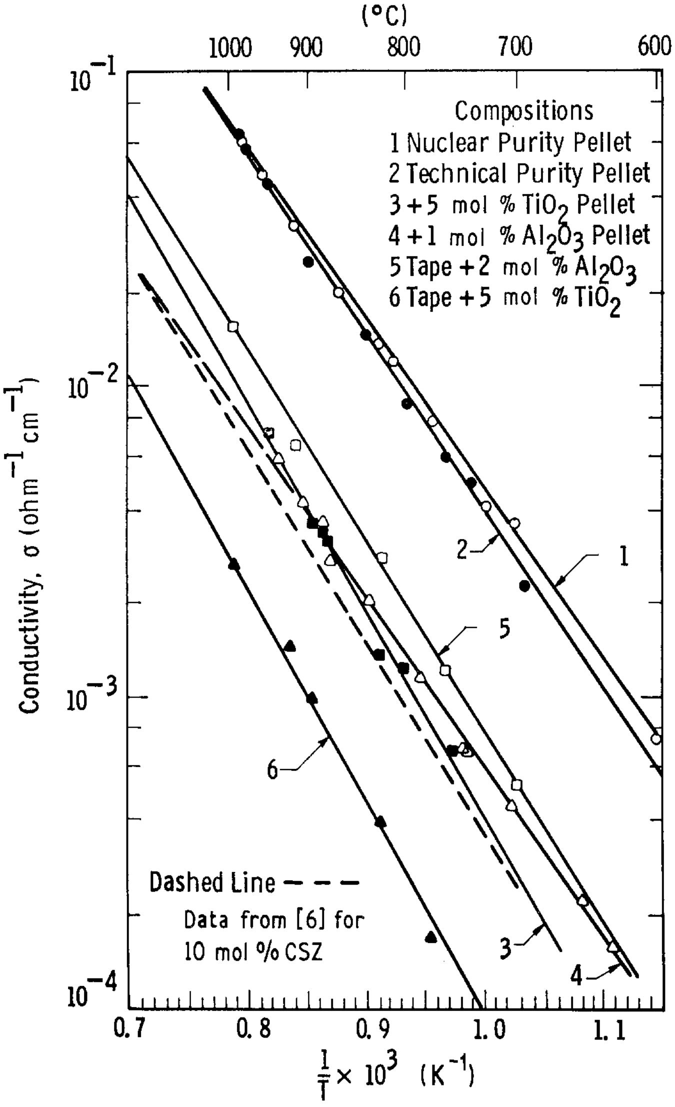

Figure 2 Conductivity data for CSZ tapes and pellets.

fired electrodes offers a substantial reduction in manufacturing costs without any sacrifice in performance. Conventional processing techniques require several thin applications of electrode material because the shrinkage that occurs during the sintering process tends to cause crazing and peeling, particularly with thick layers. Platinum is considered to be the most suitable electrode material for co-firing techniques because thermal expansion differences are small; 10.5 x 10^{-6} °C^{-1} for 5 wt% CSZ and 10.2 x 10^{-6} °C^{-1} for Pt over the temperature range 20 to 1200° C. It is necessary to match the shrinkage of the Pt electrode layer on sintering to that of the electrolyte by selection of a suitable powder particle size, and to reduce the electrode resistance but maintain adequate porosity by addition of zirconia powder. The results of the present work have shown that these parameters can be optimized to give excellent compatibility of electrode and electrolyte, and very good electrical performance.

The conductivity data showed that the tape-produced material was no different from the sintered pellets. The doped material was examined by X-ray diffraction and electron probe microanalysis in an attempt to correlate the initial conductivity drift to some change in structure. No obvious changes could be detected, although one of the tape samples showed faint diffraction lines of another phase, possibly monoclinic ZrO_2. This annealing phenomenon has also been observed previously by Tien and Subbarao [3], who observed extra diffraction lines after 1000° C anneals which were not present in 1400° C annealed CSZ samples. These extra lines were not accounted for by monoclinic or tetragonal ZrO_2, or by $CaZrO_3$, and they attributed the observations to an order–disorder transition which occurred around 1100° C. CSZ has been subjected to numerous investigations for order–disorder transitions, as summarized by Ray and Stubican [4], with the ordered phase being less conductive. These latter observations are identical to the results of the present research and the inference is that additions of Al_2O_3 and TiO_2 doping agents enhance the order–disorder transformation.

Interestingly, the lower conductivity data observed for the doped material corresponds very closely to the undoped 10 mol% (~5 wt%) CSZ conductivities reported by Strickler and Carlson [5]. This indicates that either the order–disorder transition had already occurred in their material, or else had not occurred in the undoped material tested during the present work, even though the specimens were annealed for approximately 170 h at 1000° C.

Additions of the TiO_2 and Al_2O_3 sintering aids are expected to reduce the conductivity of CSZ. The electron microprobe examinations [2] showed that the TiO_2 addition was uniformly distributed throughout the grains whereas the Al_2O_3 was concentrated at the grain boundaries. Because of the tetravalent state and ionic size of the titanium ion, a relatively high solubility is expected in the cubic CSZ lattice, as proposed by Coughanout, *et al.* [6], which would result in a reduction in the number of oxygen lattice vacancies, and hence in a decrease in conductivity. Alumina has a lower solubility in ZrO_2 than does TiO_2, and, although substitutional replacement of Zr^{4+} by Al^{3+} is expected to increase the resistivity due to reduction in anion lattice vacancies, it will be less than that for TiO_2 additions due to the difference in valence.

The pure technical grade CSZ also contained significant quantities of Si which accounts for the slightly lower conductivity than that for the nuclear grade material. With the addition of the sintering aids, a very complex interaction appears to occur, with a marked reduction in conductivity of the material with titanium while the alumina addition apparently improves the conductivity slightly over the same addition to the nuclear grade.

5. Conclusions

Differences in purity level of CSZ electrolytes cause minor variations in electrical conductivity whereas sintering aid additions show a marked reduction. TiO_2 shows a greater reduction than Al_2O_3 (which is the preferred sintering aid), and interactions with intrinsic impurities can have mixed effects. Fabrication of electrolytes by the tape process with co-fired electrodes gives similar conductivities to conventionally processed materials.

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