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Influence of Yttria Concentration upon Electrical Properties and Susceptibility to Ageing of Yttria-stabilised Zirconias

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Abstract

The most widely used electrolyte in solid oxide fuel cell (SOFC) devices is 8 mol% yttria-stablished zirconia (YSZ). Recent investigations have questioned the long term stability of this material at both the SOFC operating temperature of 1000°C and during cycling between room temperature and 1000°C. One possible method of improving the stability is by increasing the yttria concentration. Previous studies, utilising a number of different commercial YSZ powders have suggested that this may be possible; however, there were other differences between the samples in addition to yttria-content, notably impurity concentration. Thus the importance of yttria concentration has not been unambiguously demonstrated and the optimal content of yttria has not been determined. In this study, the mechanical strength and ionic conductivity of a range of ultra-pure compositions from the $(ZrO_2)_{1-x}(Y_2O_3)_x$ system close to 8 mol% yttria-stabilised zirconia, $x = 0.08$, have been investigated: 8.5 mol% YSZ was found to have comparable mechanical strength and ionic conductivity to conventional 8 mol% YSZ, but showed improved stability. On ageing at typical fuel cell operating temperatures, i.e. 1000°C, the conductivity of samples with yttria contents of 8.5 mol%, or higher, changed little; however, conductivity values for compositions with lower yttria contents decreased by 10–15%. These results strongly suggest that optimal properties are obtained for the minimum yttrium composition required to fully stabilise the cubic polymorph at the temperature of operation. © *1998 Elsevier Science Limited. All rights reserved*

1 Introduction

At fuel cell operating temperatures, the maximum ionic conductivity of yttria–zirconia ceramics is observed with an yttria content of approximately 8 mol%.[1] Although zirconia doped with 3 mol% Y_2O_3 (Y-TZP) exhibits higher mechanical strength than 8 mol% YSZ, its ionic conductivity at 1000°C is much less. It also undergoes a tetragonal-to-monoclinic transformation under hydrothermal conditions leading to physical degradation;[2] this makes its application in solid oxide fuel cell (SOFC) devices limited as water is produced at the anode when the cell is in operation. The high ionic conductivity and reasonable mechanical strength observed with the composition 8 mol% YSZ would indicate that it is an ideal material for SOFC applications. At 1000°C, however, 8 mol% YSZ appears in the two-phase region of the equilibrium phase diagram reported by Scott,[3] which implies that the cubic symmetry observed in samples of this composition prepared at temperatures in the single phase region (T > 1200°C), corresponds to a metastable phase. Annealing at 1000°C should produce a two-phase mixture of cubic and tetragonal phases; this has been observed by Ciacchi et al.[4]

Two series of commercial yttria–zirconia powders, from five different manufacturers, have recently been evaluated for use in solid oxide fuel cells.[5] These samples had yttria contents of either approximately 3 or 8 mol%. The 3 mol%, tetragonal, compositions

exhibited much lower conductivities at high temperatures and, hence were not as suitable for fuel cell operation as the cubic 8 mol% compositions. Within the 8 mol% group, some differences in ionic transport properties with small variations in composition were observed. Conductivity at 1000°C for materials with greater than 8% decreased as yttrium content increased; however, materials with compositions of less than 8 mol% yttria generally exhibited larger decreases in conductivity on annealing at 1000°C. This conductivity decrease was attributed to an increase in tetragonal phase, formed by annealing in the two phase region of the phase diagram.[5]

In a similar study of commercial zirconia powders from four different manufacturers, with yttria contents between 6 and 12 mol%, similar dependencies upon composition were reported.[6] A broad maximum in conductivity was observed for compositions of about 8 mol% yttria, and samples with yttria contents below 8 mol% were observed to age significantly at 1000°C.

Although these two studies have provided a valuable insight into the role of composition in optimising ageing resistance and conductivity, the use of several different powder sources renders firm conclusions more difficult. There are major differences between impurity contents and powder preparation routes of the different manufacturers. Although these will affect grain boundary properties to a greater extent than bulk properties, the effect on the bulk is far from insignificant and a large degree of scatter is observed in the dependence of bulk conductivity upon composition.[5,6] Indeed the authors of these two reports differ significantly in their final conclusions. Ciacchi et al.[5] claim the compositions which exhibit the highest conductivities after ageing had yttria contents of about 7·9%, whereas, Raeder et al.[6] claim that compositions with about 10 mol% have the highest conductivities after ageing.

The apparent phase instability of 8 mol% YSZ under normal fuel cell conditions is an important phenomenon, especially when one considers the required longevity of electrolytes for SOFC operation. In this study we have attempted to optimise yttria content for long term fuel cell operation. Ultrafine yttria–zirconia powders based on commercial plasma-derived zirconia with a range of compositions close to 8 mol% yttria-stabilised zirconia have been prepared and the mechanical properties, conductivity and susceptibility to ageing of these zirconias investigated. As these materials are all from the same source, the dependence of properties and stability upon composition can be studied directly without any concern about the influence of impurities. These materials are also compared with a commercial co-precipitated 8 mol% yttria-stabilised zirconia, which exhibits a similar high purity.

2 Experimental

A range of compositions in the $(ZrO_2)_{1-x}(Y_2O_3)_x$ system were prepared at Tioxide Specialties, Billingham, UK. High purity zirconia was produced by the oxidation of $ZrCl_4$ in a d.c. plasma reactor.[7] The resulting ultra-fine zirconia powder (99·999%) was intimately mixed with yttria (Meldform 99·99%), using a novel method described elsewhere,[7] to prepare yttria–zirconias containing variable contents of yttria; these samples are denoted YZ× (e.g. samples containing 7·7 mol% yttria are labelled YZ7·7). The total concentration of impurities in these yttria–zirconias was less than 0·01% in all cases. A commercially available 8 mol% YSZ, produced by a co-precipitation route (Tosoh TZ8Y), was used as a comparison, this material is also quoted as 99·99% pure. Powders were uniaxially pressed (80 MPa), pre-sintered at 1000°C for 1 h, sintered at 1500°C for 2 h, and slow-cooled, with a ramp rate of $10° \text{min}^{-1}$. Sintered densities were calculated from both geometric dimensions and by water immersion.

Phase analysis and unit cell determination were performed using a Stoe Stadi P automated X-ray diffractometer. Accurate stoichiometries of sintered samples were obtained using a Cameca SX51 electron probe micro-analysis (EPMA) instrument, operating at 15 kV and 20 μA. Twenty points were measured for each sample, using a fixed 2 μm beam, at a magnification of 10 000. Microstructures were examined using an ISI SS-400 SEM. Sintered discs for SEM were polished to a 1 rm finish, thermally etched, and carbon coated.

The flexural strength of sintered discs was determined using the biaxial disc flexure test, using a computer controlled Instron Universal Testing Machine. The flexural strength was calculated using the sample geometry, fracture load applied and the material constants.[8] Two terminal a.c. impedance measurements were performed using a Hewlett Packard 4192A impedance analyser over the frequency range 100 Hz–13 MHz. Measurements were made using platinum electrodes, in air, over the temperature range 300–1000°C.

3 Results

3.1 Sample characterisation

All reflections observed by X-ray diffraction, for as-fired samples of all compositions, could be
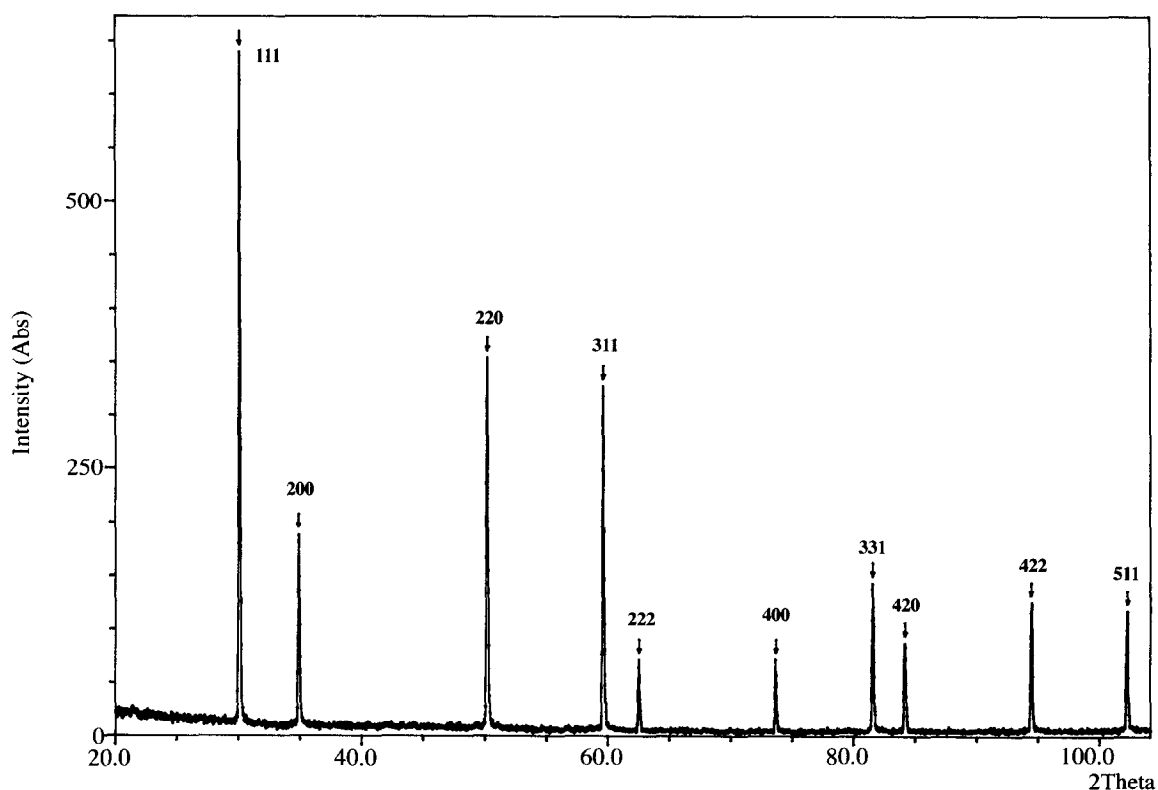
Fig. 1. X-ray diffraction pattern of as-fired Tioxide-produced 8 mol% yttria-stabilised zirconia (YZ7·7). All reflections were indexed on a cubic unit cell.

indexed on a cubic unit cell (e.g. Fig. 1). Unit cell parameters increased with yttria content in accord with literature[9] values and, assuming Vegard's Law is obeyed, confirmed the EPMA results presented in Table 1. The sharpness of the X-ray diffraction peaks indicates a very high degree of homogeneity. By considering the expected changes in peak positions with changes in composition, the materials are estimated to show less than 0·1 mol% Y_2O_3 variation in composition over more than 90% of the crystallites. Mean yttria contents for compositions close to 8 mol% Y_2O_3 obtained by EPMA, are presented in Table 1. The standard deviations reported in the EPMA results are not thought to reflect the degree of homogeneity of the samples, as such variation would be clearly apparent from X-ray powder diffraction. Instead, the standard deviations are thought to reflect morphological features such as surface roughness.

Sintered densities of the plasma-derived samples (YZ7·7, YZ8·5 and YZ9·5) were 97–99% of the

theoretical density. Co-precipitated 8 mol% YSZ (Tosoh, TZ8Y) gave sintered densities of 99%. Microstructures of samples, sintered at 1500°C for 2 h, are illustrated in Fig. 2(a)–(d). Average grain sizes (largest dimension) are presented in Table 2. The different plasma-derived samples (YZ7·7, YZ8·5 and YZ9·5) all had comparable grain sizes (Fig. 2(a)–(c)) and the size distribution was unimodal. The average grain size of TZ8Y, (Fig. 2(d)), was larger than for the plasma-derived samples and a bimodal grain size distribution was observed.

3.2 Mechanical strength

The flexural strength of samples sintered at 1500°C are listed in Table 2. TZ8Y, YZ7·7 and YZ8·5, sintered for 2 h, all have similar strengths, and compare favourably to values reported by Maenner *et al.*[10] for 8 mol% yttria. Increasing the yttria content from 7·7 to 8·5 mol% does not significantly decrease the strength of the ceramic. By contrast, an increase to 9·5 mol% yttria decreases flexural strength by 50%. YZ7·7 and YZ8·5 would appear to have comparable flexural strengths to the commercially available 8 mol% YSZ ceramics currently widely employed in SOFC prototype devices.

3.3 Ionic conductivity

A typical Arrhenius plot for 8 mol% YSZ (YZ7·7) is shown in Fig. 3. A change in activation energy associated with intra-grain oxide ion conductivity occurs at ~550°C which has been attributed to the

Table 1. Mean yttria contents (mol%) and unit cell parameters of YSZ samples sintered at 1500°C for 16 h

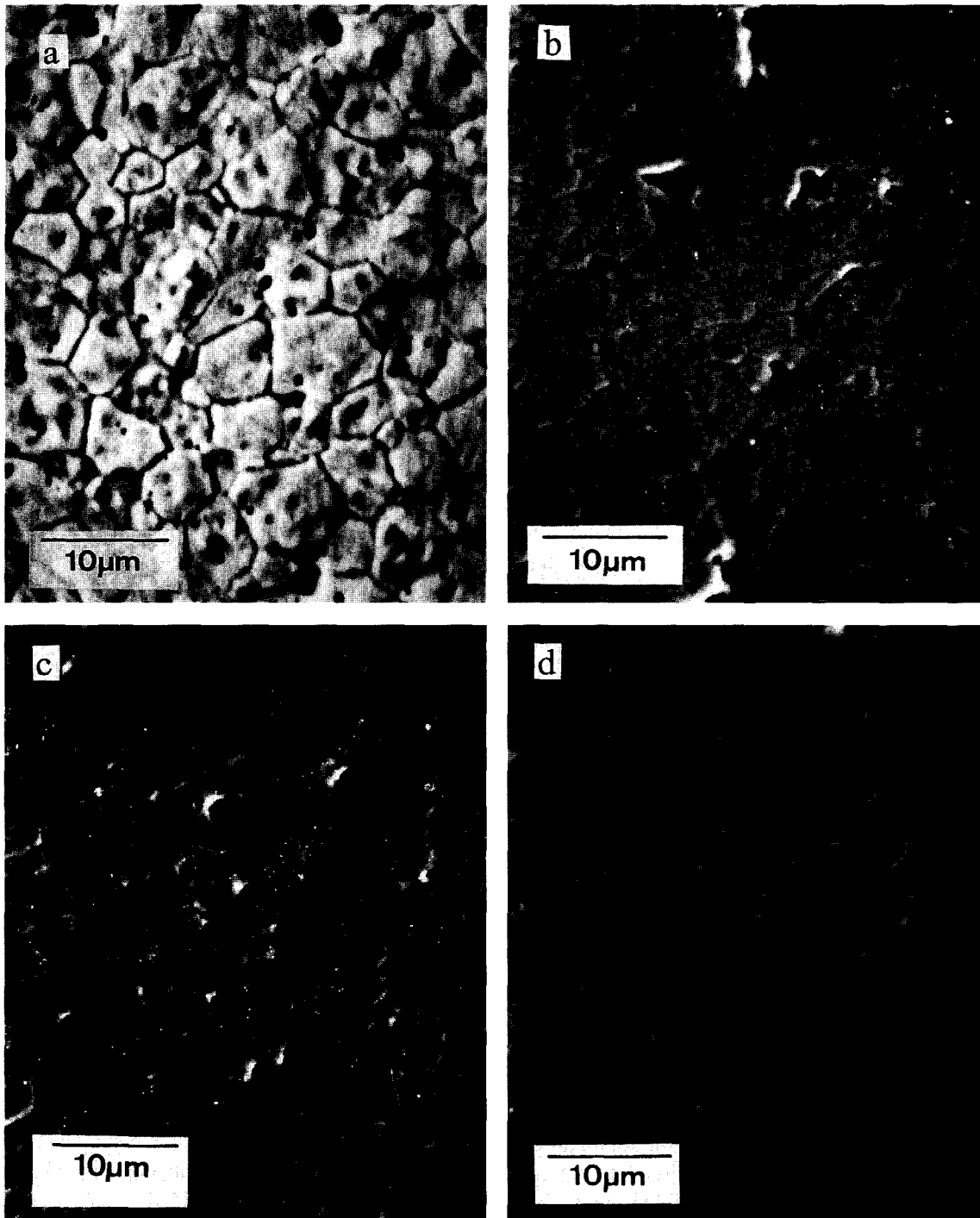| Sample	mol% Y_2O_3 16 h sintering	Unit cell edge a/Å
TZ8Y	8·1 (0·2)	5·1395(4)
YZ7·7	7·7 (0·4)	5·1374(8)
YZ8·5	8·5 (0·7)	5·1406(8)
YZ9·5	9·7 (0·4)	5·1416(4)

Fig. 2. Scanning electron micrographs of sintered samples of (a) YZ7·7, (b) YZ8·5, (c) YZ9·5 and (d) TZ8Y.

association–dissociation of defect clusters.[11,12] At low temperatures (300–450°C) two semi-circles are observed in the impedance plot; the grain boundary resistance is ~10% of the bulk resistance for all

Table 2. Average grain size and flexural strength of samples, sintered at 1500°C for 2 h

Sample	Grain size (μm)	Flexural strength (MPa)
TZ8Y	11·5	330
YZ 7·7	8·5	345
YZ 8·5	9·5	305
YZ 9·5	7	160

samples. Arrhenius plots of bulk and grain boundary conductivity are illustrated in Fig. 4 and activation energies listed in Fig. 3. At 500°C, YZ7·7 and YZ8·5 have similar bulk conductivities and are both more conductive than YZ9·5. Bulk activation energies increase with increasing yttria content, indicating an increase in defect clustering. Grain boundary conductivity decreases and activation energy increases with increasing yttria content.

Activation energies at high temperatures (>650°C) and ionic conductivities at 1000°C are presented in Tables 3 and 4, respectively. At fuel cell operating temperatures, YZ7·7, YZ8·5 and
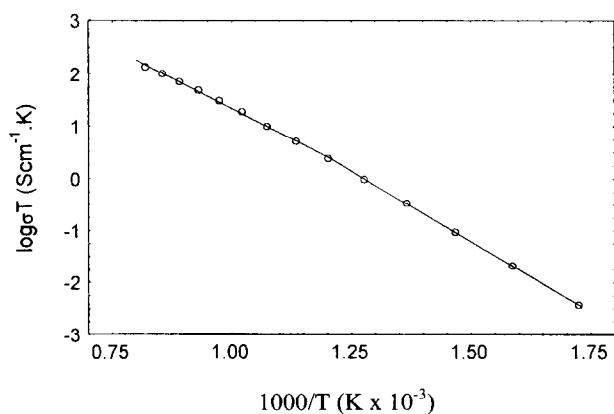
Fig. 3. A typical Arrhenius plot for cubic yttria-stabilised zirconia, showing the change in ionic conductivity as a function of temperature (YZ7·7).
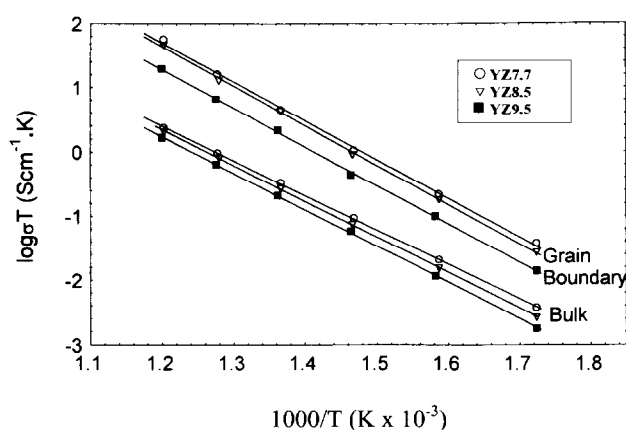

Fig. 4. Arrhenius plots of bulk and grain boundary conductivity for plasma-derived yttria-stabilised zirconia (YZ7·7, YZ8·5 and YZ9·5).

TZ8Y have similar ionic conductivities; these values are comparable to the conductivities reported by Maenner et al.[10] for 8 mol% YSZ. The conductivity of YZ9·5 is too low to be considered as an alternative to 8 mol% YSZ in SOFC applications.

The time-dependent change in conductivity of all four samples at the fuel cell operating temperature of 1000°C was determined. Figure 5 shows the change in conductivity over a period of 5000 min. At time 0, the conductivity is highest for the 7·7 mol% YSZ and decreases with increasing yttria content. Both YZ8·5 and YZ9·5 show an initial small decrease in conductivity after 2000 min, after which the conductivity appears to remain unchanged with increased annealing time. The 7·7 and 8 mol% YSZ samples (YZ7·7 and TZ8Y), however, show very different behaviour. After 2000–2750 min, the conductivity of both samples has become similar to that of YZ8·5. Prolonged annealing produces a further decrease in conductivity and, after 5000 min, YZ7·7 and TZ8Y have lower conductivity than YZ8·5. The conductivity of YZ7·7 decreases the most, Table 5. YZ9·5 shows the smallest change in conductivity after annealing at

Table 3. Bulk and grain boundary activation energies of conduction

Sample	E_A (bulk) $T < 650°C$ (eV)	E_A (bulk) $T > 650°C$ (eV)	E_A (g.b.) (eV)
TZ8Y	1·09	0·93	1·13
YZ7·7	1·08	0·92	1·16
YZ8·5	1·11	0·93	1·18
YZ9·5	1·14	0·95	1·21

Table 4. Ionic conductivities at 1000°C of YSZ samples, sintered at 1500°C for 2 h

Sample	Ionic conductivity (Sm^{-1})
TZ8Y	15·6
YZ7·7	16·0
YZ8·5	14·9
YZ9·5	10·7

1000°C for 5000 min, but its conductivity is much lower than the other samples.

To illustrate the shift in the optimum composition for maximum conductivity after annealing, the time-dependent change in conductivity of YSZ samples containing between 5 and 11 mol% yttria was measured at 1000°C. Figure 6 shows the ionic conductivity of unannealed and 5000 min annealed YSZ samples as a function of yttria content; the maximum conductivity shifts from 7·7 to 8·5 mol% yttria after annealing. Samples with 7 mol% yttria always cracked during cooling and so their conductivities could not be measured. This cracking was unavoidable because the cubic/(cubic and tetragonal) phase boundary for 7 mol% is located at around 100°C below the 1500°C sintering temperature that we used in these comparative studies.
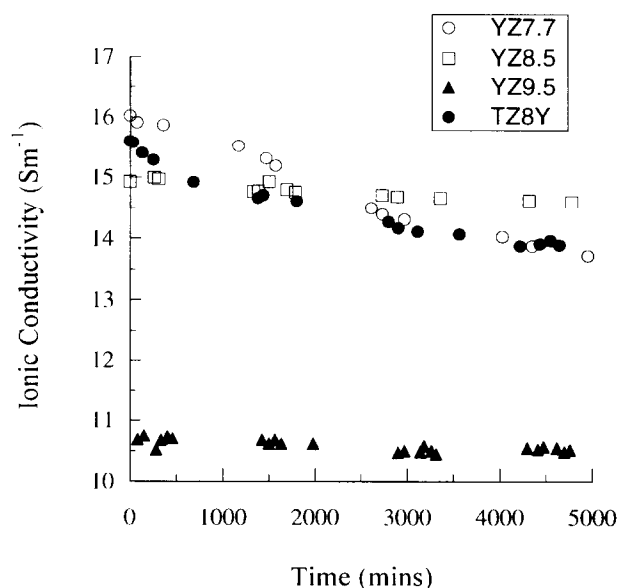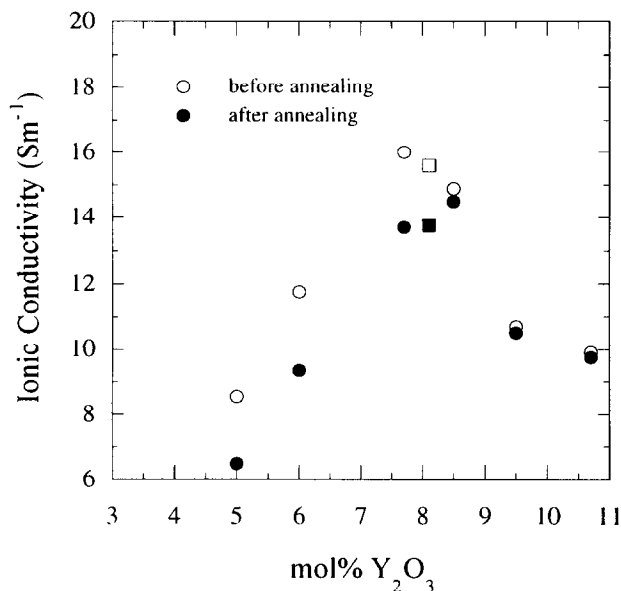

Fig. 5. The time-dependent decrease in ionic conductivity of YSZ samples at 1000°C between 0 and 5000 min.

Table 5. Ionic conductivities at 1000°C of YSZ samples before and after annealing for 5000 min

Sample	$\sigma(Sm^{-1})$ at 1000°C	$\sigma(Sm^{-1})$ at 1000°C, after 5000 min	% decrease
TZ8Y	15·6	13·75	11·8
YZ7·7	16·0	13·7	14·2
YZ8·5	14·9	14·5	2·4
YZ9·5	10·7	10·5	1·7

Fig. 6. The change in ionic conductivity as a function of yttria content of (○, ●) unannealed and annealed plasma-derived 5–11 mol% and (■, □) co-precipitated 8 mol% yttria-stabilised zirconia at 1000°C. The maximum conductivity shifts from 7·7 to 8·5 mol% yttria after annealing.

4 Discussion

In this study, we have found that increasing the yttria content of YSZ to 8·5 mol% (YZ8·5) produces a ceramic with very similar flexural strength to 8 mol% YSZ (YZ7·7 and TZ8Y); however, on increasing from 8·5 to 9·5 mol% yttria (YZ9·5), strength decreased dramatically. The ionic conductivity of the plasma-derived 7·7 mol% YZ7·7 at 1000°C was similar to that of the co-precipitated 8·0 mol% TZ8Y, which is widely used in SOFC research, and compared favourably to the conductivity of 8 mol% YSZ prepared by other routes.[4,10]

Previous reports indicate that the maximum ionic conductivity in YSZ is observed with compositions containing around 8 mol% yttria, with conductivity dropping sharply above and below this composition.[1,13] This study indicates that the lower the yttrium content in the cubic phase the higher the conductivity (Table 4) although the difference in conductivity between 7·7 and 8·5 mol%

yttria content is not that large. Phase stability of YSZ ceramic electrolytes is of key importance to long term SOFC applications; cubic 7·7 mol% YSZ is certainly only metastable at 1000°C and even 8·0 mol% seems to be in a two phase region at 1000°C according to Scott's diagram.[3] Ciacchi et al.'s[5] study of commercial 7·5–8·8 mol% YSZ powders showed that samples with lower yttria contents showed the greatest decrease in conductivity after annealing at 1000°C for 5000 min. This decrease in conductivity was attributed to the precipitation of a less conductive tetragonal phase, in accordance with the equilibrium phase diagram at 1000°C. The sample with the highest yttria content showed the smallest drop in conductivity. However, the conductivity of this sample after annealing was still lower than all the other samples in their study; this may be due to the high level of impurities and relatively low density (93% of the theoretical density) of the high yttria sample. The wide variety of powders studied, particularly with regard to impurity levels made direct comparisons difficult.

In this study, all samples had no detectable impurity contents and comparable densities. The conductivity of samples containing ~8 mol% yttria (TZ8Y and YZ7·7) showed a large decrease (10 and 15%, respectively) after annealing at 1000°C for 5000 min. This decrease is similar to that observed by Ciacchi and is also thought to be due to the precipitation of a tetragonal phase.

Samples containing 8·5 and 9·5 mol% yttria showed a minimal drop in conductivity after 5000 min (~1%), indicating that defect aggregation is not the main cause of ageing in this study as samples with higher vacancy contents should be more susceptible to defect aggregation. Previous studies have described ageing in YSZ ceramics containing concentrations of Y_2O_3 greater than 10 mol%[14,15] and have attributed this, in part, to defect aggregation. It should be noted, however, that the principal cause of ageing in these studies was due to changes in the grain boundary conductivity, probably due to segregation of impurities at the grain boundaries. Compositions of 8·5 and 9·5 mol% YSZ both lie in the cubic region of the phase diagram at 1000°C, so at equilibrium, a less conductive tetragonal phase would not be present. The slight decrease in conductivity in these samples is most likely to be due to sintering of the platinum electrodes causing a decrease in the contact area.

In contrast to the work of Ciacchi et al.,[5] this study indicated that after annealing samples at 1000°C for 5000 min, the conductivity of 8·5 mol% YSZ (YZ8·5) was greater than both 8 mol% YSZs (YZ7·7 and TZ8Y). This clearly reverses the trend believed to occur where the maximum conductivity

is obtained with 8 mol% YSZ.[1,13] A similar finding was reported by Raeder *et al.* although these workers claimed that after ageing 10 mol% had the highest conductivity.

5 Conclusions

The ionic conductivity and mechanical strength of a 7·7 mol% yttria-stabilised (YZ7·7), prepared by the yttria coating of a plasma-derived zirconia, compares well with a commercially available co-precipitated 8 mol% YSZ (TZ8Y). After annealing at 1000°C for 5000 min, the conductivity of 8·5 mol% YSZ is greater than that of both 8 mol% YSZs. This has major implications for fuel cell applications where decreases in cell performance may occur due to a drop in electrolyte conductivity. Clearly, a small increase in the amount of dopant added can be beneficial to the long term properties of a YSZ electrolyte employed in SOFC devices operating at 1000°C. The comparable mechanical strength and ionic conductivity, and the enhanced phase stability, makes 8·5 mol% YSZ a promising alternative to the currently employed 8 mol% YSZ for use as a solid electrolyte in SOFC devices.

To maximise conductivity, it seems that the minimum yttrium content necessary to thermodynamically stabilise the cubic phase at operating temperatures is required. If higher yttria concentrations are utilised conductivity will be lower, and if lower concentrations are used, so that the cubic phase is only kinetically stable, ageing will occur and the conductivity will decrease.

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