YTTRIA CO-DOPING OF SCANDIA-ZIRCONIA ELECTROLYTES FOR SOFCs

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ABSTRACT

Scandia stabilised zirconias offer much better performance than the conventional yttria stabilised materials and now it seems that availability and cost may not be hugely problematic. This offers a very important way forward to fuel cell manufacturing. It is shown here that a small addition of 2 mol% yttria to scandia stabilised zirconia results in formation of the cubic phase and so avoids major phase changes in scandia only substituted zirconia, which we believe is likely to be detrimental to long term electrolyte stability. This addition of yttria can be achieved without significant impairment of the electrical conductivity of the scandia stabilised zirconia. Samples which are cubic throughout the studied temperature range, i.e. either effectively quenched scandia only or yttria co-doped show two linear conductivity regions in Arrhenius conductivity plots. Importantly the low temperature activation energy decreases and the high temperature activation energy increases as yttrium content increases and scandium content decreases. This correlates with short-range order effects observed by neutron diffraction. Thus we have identified a new range of composition for use in solid oxide fuel cell electrolytes, which exhibits a good compromise between phase stability and electrical properties.

INTRODUCTION

Solid oxide fuel cells offer clean generation of electricity at high efficiencies. Current developments are based upon an yttria-stabilised zirconia electrolyte which functions very well at temperatures in the 850-1000°C range for unsupported electrolytes and at temperatures as low as 700°C for supported thin films. Two design concepts predominate, the more expensive tubular design and the simpler planar design. The major weakness of the planar concept relates to interconnect and sealing problems. If a lower temperature electrolyte could be achieved, then much cheaper materials could be utilised for interconnects (steel, in fact) and the cost effectiveness of the planar design, in particular could be greatly enhanced. One other concern about the electrolyte that should be highlighted is stability; the tetragonal modification of yttria-stabilised zirconia undergoes a catastrophic transformation under hydrothermal conditions at about 300°C [1]. Most commercial cubic zirconias are actually prepared with the composition 8mol%Y2O3/92%ZrO2, which strictly is just inside the two-phase cubic/tetragonal zirconia phase field below 1000°C [2]. This means that on ageing these electrolytes at fuel conditions, tetragonal precipitates occur reducing conductivity [3,4]. Furthermore, on cycling this electrolyte between room temperature and operating temperature in the...
presence of water (a product of fuel cell operation) degradation and failure are highly likely due to the presence of the tetragonal form. Any compositional inhomogeneity, as we have observed in some of the "highest" quality commercial products, means that failure will occur. These problems can be reduced or even avoided if slightly higher yttria compositions are utilized [4].

Scandia-stabilised zirconia offers much higher conductivity than yttria-stabilised zirconia at 1000°C (x3) with a larger enhancement at lower temperature due to the lower activation energy (0.65 eV vs. 0.95 eV) [5]; however, it has not been viewed as a serious alternative due to cost until recently. This has now changed with the increase in availability of scandia from Russia and China; presently, scandia is perhaps only 4 times as expensive per gram or approaching 2 times as costly per mole as yttria and it does seem that prices could decrease further. Although scandia-stabilised zirconias could be viewed as offering a route to even lower temperatures of operation than can be achieved using supported yttria-stabilised thin film electrolyte designs, we see the primary advantages of scandia systems as a dramatic decrease in internal cell resistance and offering more robust designs for low temperature operation. It is widely recognised in the field that once a low enough temperature of operation has been achieved to allow low cost steel interconnects to be utilised and sealing problems to be minimised, then there is no advantage for a further decrease in operating temperatures as most design concepts benefit from high temperatures, e.g. SOFC-gas turbine, and at these temperatures the internal reforming of hydrocarbons remains an attractive possibility.

The $Y_2O_3$-$Sc_2O_3$-$ZrO_2$ system with 8 mol% stabilising dopant content has been studied by Ciacchi and Badwal [6] and more recently with 9 mol% [7]. Samples of this system were prepared by co-precipitation method and sintered at 1750°C [6] and 1500°C [7]. According to XRD analysis all sintered specimens were in the two-phase field: cubic fluorite and tetragonal (t'-phase). The conductivity of the ternary compositions studied was found to be between those of the binary systems; however, these sintered compositions appear to be not very stable during extended annealing. The conductivity of samples decreased with time at 1000°C. The authors explain these results from the decomposition of t'-phase and the precipitation of tetragonal $ZrO_2$ from the cubic matrix for scandia-rich compositions. In yttria-rich compositions tetragonal $ZrO_2$ precipitates to the cubic phase as a result of yttrium redistribution in the cubic phase.

**EXPERIMENTAL**

Samples in the ternary system $(Y_2O_3)_x(Sc_2O_3)_y(ZrO_2)_{1-x-y}$ were prepared by solid state reaction of oxide powders: scandia powder (Stanford Material Corporation, 99.99% purity), zirconia powder (Fluka, 99% purity) and yttria powder (Alfa Aesar, 99.9% purity). The starting oxides were mixed with acetone and milled in a Fritsch planetary ball mill ‘pulverisette 7’ using zirconia containers and zirconia balls. Dried powders were pressed into pellets of diameter 13 mm and thickness 2-2.5 mm at 250 MPa. The pressed pellets were sintered at 1600°C for 16 hours and then quenched to room temperature from 1000°C.

The relative densities were calculated from pellet geometry and mass and were in the range of 88-92%, which are reasonable for solid state powder prepared samples. A Stoe
Stadi P X-ray diffractometer (10°-90° 2θ, step size 0.02° 2θ, CuKα radiation) was used to determine crystalline structures and unit cell parameters, utilising an external Si standard for calibration. Ionic conductivities were measured using a Solartron 1260 frequency response analyser in the frequency range 6 MHz to 0.1 Hz at temperatures 300-1000°C with Pt paste electrodes.

Sintered samples for SEM were polished, thermally etched and gold coated. The average grain sizes were determined by the linear intercept length method.

RESULTS AND DISCUSSION

Phase formation in the Sc2O3-ZrO2 system with scandia contents between 5.0 and 15.0 mol% shows monoclinic, rhombohedral and cubic phases. Compositions with Sc2O3 content from 8 to 12 mol% are members of a fluoride-type cubic solid solution at 1000°C. Impedance spectroscopy was applied to study the ionic conductivity. The best ionic conductivity was observed for the compositions with 10 and 11 mol% Sc2O3. Long time annealing performed on samples with scandia content between 9 and 12 mol% has been investigated at 800°C for 1500 hours. Samples with 9 and 12 mol% scandia showed significant decrease in conductivity. The 10 and 11 mol% scandia samples exhibit high electrical conductivities and reasonable stabilities at 800°C (figure 1); however phase changes that would occur at temperatures below are expected to cause problems during thermal cycling even for 10 and 11% scandia.

Figure 1. Conductivity degradation in Sc2O3 - ZrO2 system, containing Sc2O3 from 9 to 12 mol% after long term annealing at 800 °C for about 1500 hours.

The effect of yttria co-doping of scandia zirconia on stabilisation and ionic conductivity has been investigated focusing upon higher total doping levels than 8 mol%. Compositions in the ternary system \((Y_2O_3)_{x}(Sc_2O_3)_{(11-x)}(ZrO_2)_{89} (YxSc11-xZr89, x = 0-11)\) were prepared by solid state reaction and characterised by XRD, SEM and impedance spectroscopy. The electrical conductivity was studied as a function of temperature. The stability of the electrolyte materials was examined at the intermediate solid oxide fuel cell
temperature of 800°C for up to 1500 hours. The contribution of the bulk and grain boundary resistivity of sintered and long term annealed compositions to total resistivity was estimated. Yttria additions were found to improve the phase stability of scandia stabilised zirconia. Even 1 mol% Y$_2$O$_3$ addition eliminates the rhombohedral phase (Sc$_2$Zr$_7$O$_{17}$, the beta-phase) and stabilises the cubic structure at room temperature. The best overall ionic conductivity was observed for compositions containing 2 mol% Y$_2$O$_3$. The 1 and 2 mol% Y$_2$O$_3$ compositions exhibit high electrical conductivities and good stabilities. Typically two linear regions were observed in the Arrhenius conductivity plot (figure 2). The lower temperature region exhibited an activation energy of 1.3 eV and the high temperature region 0.75 eV. The difference between these activation energies decreases as yttria content increases and thus we attribute this change to a short range ordering effect rather than simple near neighbour associations. As Sc better matches the host lattice in terms of size, it would be expected to have a smaller energy of binary defect association.

![Figure 2. Temperature dependences of conductivity of the Sc11Zr89 and Y1Sc10Zr89 compositions sintered at 1600 C for 16 hours.](image)

Ionic conductivity and microstructure of the compositions in the (Y$_2$O$_3$)$_1$-(Sc$_2$O$_3$)$_x$-(ZrO$_2$)$_{99-x}$ and (Y$_2$O$_3$)$_2$-(Sc$_2$O$_3$)$_x$-(ZrO$_2$)$_{98-x}$ systems with total dopant content in the range 7-11 mol% has been investigated as functions of temperature (300-1000 °C) with XRD, SEM and impedance spectroscopy. It has been demonstrated that the introduction of 8-11 mol% additions of total yttria and scandia fully stabilise the cubic phase to lower temperature and eliminate the cubic-rhombohedral phase transition for both levels of yttria content. Introduction of 2 mol% yttria into scandia stabilised zirconia results in an increased unit cell parameter and decreased grain size compared to the introduction of 1 mol% yttria. Doping of scandia-zirconia with 2 mol% yttria is preferable to doping with 1 mol% yttria and leads to higher ionic conductivity. At lower temperatures, e.g. figure 3, this is related to a lower activation energy for ionic transport at such temperatures. All sintered samples from the (Y$_2$O$_3$)$_2$-(Sc$_2$O$_3$)$_x$-(ZrO$_2$)$_{98-x}$ system showed high bulk conductivity with a small contribution from the grain boundary resistivity. The grain boundary resistivity in the (Y$_2$O$_3$)$_1$-(Sc$_2$O$_3$)$_x$-(ZrO$_2$)$_{99-x}$ system was more significant and comparable with the value of bulk resistivity at 400°C. The enhancement of electrical properties and the improving of the ceramic microstructure samples in the (Y$_2$O$_3$)-
(Sc₂O₅)-(ZrO₂) system doped with 2 mol% yttria compared with samples in the (Y₂O₃)-(Sc₂O₅)-(ZrO₂) system doped with 1 mol% yttria is not simply due to microstructure and is indicative of improvements in the conduction of both the bulk and intergrain regions. This may reflect that there is still some small degree of secondary phase formation with only 1 mol% yttria co-dopant and so 1 mol% Y₂O₃ doped samples show similar decreased conductivities to those of scandia zirconias that have not been rapidly quenched to retain complete cubic structure.

**Figure 3. Impedance spectra plots of Y₁Sc₉Zr₉₀ and Y₂Sc₈Zr₉₀ samples, recorded at 353 °C.**

Neutron diffraction experiments were concerned with different compositions of the binary solid solution join, Zr₀.₈₂Y₀.₁₈₋ₓScₓO₁.₉, over the temperature range, 170-700 K; all with an overall dopant concentration of 18 atom% but with different Sc:Y ratios. Two types of scattering were observed: narrow peaks arising from the fluorite Bragg reflections and broad peaks that were observed at some forbidden cubic fluorite lattice positions, i.e. hkl: h+k+l=2n; 0kl: k,l =2n; hhl: h+l=2n and h00: h=2n. The diffuse scattering is hence likely to originate mainly from localised tetragonal distortions. Diffuse scattering features were observed in all cases, however, they were less pronounced at higher temperatures. This suggests that the localised tetragonal distortion is reduced on heating. The magnitude of diffuse scattering also increases with increasing scandium dopant content. Isotropic temperature factors of oxygens are large, indicating significant distortion of the oxygen lattice, and increase linearly with temperature in the investigated range. At each temperature, temperature factors (figure 4) are of the same order of magnitude for all investigated compositions.

**Figure 4. Oxygen temperature factors for composition Zr₀.₈₂Sc₀.₀₉Y₀.₀₉O₁.₉₁ as a function of temperature.**
CONCLUSIONS

Low levels of yttria co-doping stabilise the cubic phase of scandia stabilized zirconia in the 10-11 mol% total sesquioxide dopant regime. Although the high temperature conductivity is slightly reduced in co-doped samples compared to the scandia only doped, the avoidance of macroscopic phase transitions provides better stability on thermal cycling and gives better reproducibility. Although long-range order is avoided on yttria doping, all compositions show significant short-range order, most probably due to microdomain formation principally based on the anion sublattice. This short-range order weakens on yttria co-doping decreasing the activation energy in the lower temperature short range-ordered regime. Yttria co-doping, however increases activation energy in the high temperature disordered regime. This means that for a given total dopant level, high scandia content samples offer the greatest conductivity enhancement over lower Scandia content samples in an intermediate temperature range, with less or even negative enhancement at high or low temperatures.

ACKNOWLEDGMENTS

The authors would like to thank EPSRC for support and the CLRC for provision of beamtime at ISIS.

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