Characterisation of Submicron-Grain Sized Yttria-Stabilised Zirconia Electrolyte for SOFCs

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Abstract: This paper investigates the effect of grain size within the nano to micron regime on ionic conductivity for yttria stabilised zirconia (YSZ) with various yttria levels. The samples were made using either slip casting or die pressing routes and were characterised via the use of 4-point electrical conductivity, AC impedance, high resolution transmission electron microscopy (HRTEM) and a field emission gun scanning electron microscope (FEGSEM). Little variation in ionic conductivity was noted over the range of grain sizes examined; rather the yttria content had the largest effect. The greatest variation was noted between the 3 mol% YSZ and 8 mol% YSZ where the conductivity was seen to vary by ~65% at 850 °C. This work forms part of an investigation into the potential use of fine grained zirconias as electrolytes in solid oxide fuel cell (SOFC) applications.

Key words: Yttria-stabilised zirconia, submicron YSZ, nanocrystalline YSZ, solid oxide fuel cell, electrolyte, ionic conductivity, TEM.

1. Introduction

The call for energy generation has increased drastically over recent years. In particular, fuel cell technology is one of the most promising and novel approaches towards a greener, cleaner and quieter environment. Among these, solid oxide fuel cells (SOFCs) have gained in popularity due to their high efficiency, the use of inexpensive catalyst materials and the flexibility to be able to use different fuels. SOFCs are conversion devices that electrochemically convert fuel and an oxidant into electrical energy without combustion [1, 2]. Yttria-stabilised zirconia (YSZ) is the most common electrolyte material used due to its combination of useful properties, viz. high chemical and thermal stability and high ionic conductivity over a wide range of conditions. However, an existing restriction on the development and

application of SOFCs remains their relatively high operating temperature, 800-1000 °C, which is needed to achieve the required level of ionic conductivity. This high operating temperature leads to structural problems, such as electrode sintering and interfacial diffusion between the electrolyte and electrodes [3, 4]. Provided they were mechanically strong enough, thinner electrodes would reduce the ohmic loss during cell operation allowing a lower operating temperature to be used. One way that this might be achieved would be through the use of a finer grain sized electrolyte layer. Nano ceramics are reported to exhibit increased strength, hardness and toughness, reduced elastic modulus and ductility, enhanced diffusivity, higher specific heat capacity and thermal expansion coefficient (CTE) and superior soft magnetic properties [5]. In addition, nano YSZ requires lower sintering temperatures, allowing co-sintering with lower temperature metals to take place, which aid in lowering production costs [6, 7]. However, a key requirement is that the ionic conductivity is not deleteriously affected

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by the very fine grain size. Although previous work has suggested that the grain boundary conductivity in nano YSZ can be enhanced by 1-2 orders of magnitude compared to micron-grain sized YSZ [8], further work is needed to investigate the effect of grain size and yttria content on the ionic conductivity. This paper forms an 'interim report' covering the work done to date on the effect of both grain size and yttria content on the ionic conductivity in YSZ for SOFC applications.

2. Experiment

2.1 Specimen Preparation

The materials examined in this study range from nano 3 mol% YSZ (3YSZ), obtained as an aqueous nanosuspension, through submicron grain sized 3YSZ powder to micron grain sized 8YSZ. All of them were obtained from MEL Chemicals, Manchester, UK. The precursor nanosuspension, which contained 3YSZ nanoparticles with a mean size of ~18 nm, was concentrated from ~7 vol% to ~20 vol% using a procedure that has been described elsewhere [9] and then slip cast using plaster of paris moulds to form discs measuring 4 mm diameter by 3 mm thick. Full details of the slip casting process have been provided elsewhere [7] and the green densities achieved were about 57% of theoretical. The 8YSZ powder was die pressed uniaxially into pellets measuring 8 mm in diameter by 5 mm thick using a hardened steel die and a pressure of 120 MPa. The 3YSZ powder was both slip cast and die pressed into pellets measuring 8 mm in diameter by 3 mm thick. The slip cast nano YSZ were sintered using a two-step sintering cycle where the specimens were heated initially to 1150 °C and held for 1 min before being cooled down to 1050 °C where they were held for 10 h to achieve a mean grain size of approximately 100 nm. Further information on the application of two-step sintering to nano YSZ may be found elsewhere [10]. The 8YSZ pellets were sintered using a single stage sintering process involving holding them for 1 hr at 1550 °C, whilst the 3YSZ pellets made

from submicron grain sized powder were sintered for 1 hr at 1350 °C. The grain size of the 3YSZ was increased to 200 and 300 nm by separate annealing steps performed on the die pressed samples by holding for 1 and 5 h at 1350 °C respectively. All sintering was performed using a conventional radiant furnace (Carbolite UK Ltd, Sheffield, UK).

2.2 Microstructure Characterisation

X-ray diffraction (XRD) profiles of the samples were measured at room temperature using a powder diffractometer system (Model D8, Bruker AXS Inc., Madison, USA) and recorded using CuK α radiation using 40 kV and 30 mA at a slit width of 1°. A LEO 1530 VP (Carl Zeiss, Cambridge, UK) scanning electron microscope (SEM) fitted with a field emission gun (FEG) was utilised to collect images of the sintered microstructures at varying magnifications between 1,000 and 25,000. The FEGSEM samples underwent polishing with a 3 μ m diamond paste before being thermally etched for 6 minutes at 50 °C below the sintering temperature in air. The average grain sizes were measured using the linear intercept method [11], Eq. (1),

$$D = \frac{L \cdot A1}{M \cdot N} \quad (1)$$

where D is the mean grain size in μ m, L is the length of line in μ m, $A1$ is the shape correction factor, taken as 1.5, M is the magnification and N is the number of intercepts. High resolution transmission electron microscope (HRTEM) investigations of the sample grains and grain boundaries were undertaken at 200 kV (Tecnai F20 TEM, FEI, Hillsboro, Oregon, USA). Nanoprobe EDS measurements were also performed to look quantitatively for segregation of the yttrium ions across the grains and grain boundaries. For the latter, specimen preparation was undertaken using a dual beam focused ion-beam (FIB) using a Strata 205 (FEI, Hillsboro, Oregon, USA).

2.3 Conductivity Measurements

Impedance spectroscopy measurements were performed

Table 1 Details of samples used in this study.

Specimen code	Peak temperature T_1 (°C)	Temperature T_2 (°C)	Relative density (%)	Mean grain size (nm)
3YSZ100sc*	1100	1050	99.0 ± 0.5	100 ± 10
3YSZ200sc	1350	-	99.0 ± 0.5	200 ± 10
3YSZ200dp	1350	-	99.0 ± 0.5	200 ± 10
3YSZ300dp+a*	1350	-	99.0 ± 0.5	300 ± 10
8YSZ3000dp	1550	-	98.0 ± 0.5	3000 ± 0.10

*where 3YSZ100sc = 3YSZ with 100 nm mean grain size and made by slip casting; 3YSZ300dp+a = 3YSZ with 300 nm mean grain size and made by die pressing with annealing to increase the grain size. Other specimen codes are based on the same principles.

over the frequency range of 1 MHz to 1 Hz and with an amplitude signal of 100 mV (1260 FRA, Solartron, Farnborough, Hampshire, UK). Measurements were carried out from 250-450 °C in an air atmosphere; the temperature being monitored by a thermocouple. The electrodes were fabricated by applying platinum paste on both faces of the pellets followed by annealing at 850 °C for 1 h in air. The grain and grain boundary dc resistivities were determined by fitting equivalent circuits to the semi-circle arcs on the complex impedance spectra. In order to ensure reproducibility and repeatability of the measurements, at least two specimens were measured at each grain size.

3. Results and Discussion

3.1 Density Measurements

Table 1 shows sintering conditions, relative densities and mean grain sizes of the samples prepared. It can be seen that the relative sintered densities of the specimens were between 97.5-99.5% based on the Archimedes principle using mercury whilst the grain sizes, revealed using electron microscopy and image analysis, ranged from 100 to 300 nm for the 3YSZ samples made from the nanosuspension, ~200 nm for the 3YSZ samples made from powder and were ~3000 nm for the 8YSZ. Further work is currently underway within this research programme to produce a full range of samples with mean grain sizes from ~70 -3000 nm for the 3YSZ and 8YSZ and also to create samples with a ~100 nm mean grain size from 5 and 10 mol% YSZ.

3.2 XRD Spectra

The XRD spectra for the 3YSZ and 8YSZ powders are presented in Fig. 1 together with the characteristics of tetragonal 3YSZ and cubic 8YSZ, respectively. As expected, there is no indication of the existence of secondary phases though it should be noted that the resolution of the technique is only ~3-4%.

3.3 Micro/Nanostructure Analysis

Fig. 2 shows the nano/microstructures of the sintered specimens prepared for this study, it can be seen how the annealing schedule was successful in coarsening the

Fig. 1 XRD spectra for 3YSZ and 8YSZ specimens are shown in comparison with the reported tetragonal and cubic spectra for YSZ [12, 13].

Fig. 2 FEGSEM micrographs of (a) 3YSZ100sc, (b) 3YSZ200dp and (c) 3YSZ300dp+a showing mean grain sizes of ~100, 200 and 300 nm respectively.

microstructure significantly. Fig. 3 shows the microstructure for the 8YSZ3000dp samples; it is clearly much coarser and bimodal in nature. When 3YSZ is sintered at $<1300\text{ }^{\circ}\text{C}$ the yttria distribution remains uniform and all of the grains are tetragonal. However, at sintering temperatures $\geq 1500\text{ }^{\circ}\text{C}$ a heterogeneous distribution of yttria forms at the grain boundaries and triple points leading to the formation of some cubic grains [14]. The yttria content is reported to vary from ~6 mol% at the grain boundaries to ~2 mol% at the grain interiors for a tetragonal-tetragonal grain boundary, and from ~1 mol% to ~8 mol% across a tetragonal-cubic grain boundary, with ~6 mol% at the grain boundary itself. Between $1300\text{--}1500\text{ }^{\circ}\text{C}$ an intermediate situation develops. For the submicron 3YSZ samples, analysis revealed that the yttria content varied from ~2.3 mol% at the grain centre to ~7.4 mol% at the grain boundaries, Fig. 4. It was also observed that in the region between the grain boundary and the grain centre the yttria content was even lower, ~1.9 mol%. It is assumed that yttria from the regions near the grain boundaries preferentially migrated to the grain boundaries, generating areas that were even lower in yttria content than at the grain centre. It is also assumed that this variation in yttria content between the grain centre and regions between the grain centre and grain boundary would disappear if the sample were kept for a longer period of time at the sintering temperature. The 3YSZ100sc samples in the present study were sintered at temperatures much lower than $1300\text{ }^{\circ}\text{C}$ and the yttria content was found to be uniform

Fig. 3 FEGSEM micrograph of 8YSZ3000dp with a mean grain size of ~3 μm .

Fig. 4 HRTEM image of a 3YSZ sample. The yttria content, in mol%, at various locations is indicated [15].

across the grains and grain boundaries.

Fig. 5a shows a typical HRTEM micrograph of the grain boundary structure of the 3YSZ200dp. There is no indication of amorphous or secondary phases existing along the grain boundary, nor was any presence found of impurities or excessive segregation of yttria along the grain boundary. However, in contrast a ‘necklace-like’ structure was observed along the grain boundary in the 8YSZ3000dp samples, Figs. 5b

Fig. 5 HRTEM micrographs on (a) 3YSZ200dp and (b) & (c) 8YSZ3000dp.

and 5c. When this was observed previously, it was believed to be due to impurities developed from the presence of alkali silicate/nickel in the structure since the study was based on the nickel/YSZ interface [16]. However no impurities were observed from the EDAX in this study.

3.4 Conductivity Properties

AC impedance spectroscopy was used to investigate the transport properties of the grains and grain boundaries with respect to mean sample grain size. The total resistance of the electrolyte is given by Eq. (2) [17]:

$$R_t = R_g + R_{gb} \quad (2)$$

where R_t is the total resistance (Ω), R_g is the grain resistance (Ω) and R_{gb} is the grain boundary resistance (Ω). Total conductivity is based on Eq. (3):

$$\sigma = \frac{1}{R} \cdot \frac{L}{A} \quad (3)$$

where L is the specimen thickness (cm) and A is the specimen area (cm^2). The conductivity data were plotted

using an Arrhenius Eq. (4):

$$\sigma = \frac{\sigma_0}{T} \exp\left(-\frac{E_a}{kT}\right) \quad (4)$$

and E_a is the activation energy of electrical conduction (eV), k is the Boltzman's constant (eV/K), T is the absolute temperature (K) and σ_0 is the constant pre-exponential factor. The activation energies were calculated from the slope of linearised Arrhenius plots.

The Arrhenius plot in Fig. 6a suggests that, within the measured temperature range, the total activation energies for the different samples were very similar. Table 2 shows the values obtained. Total conductivities of the specimens were measured in the range 250–450 °C using AC impedance, Fig. 6b. Whilst the 3 different grain sizes of 3YSZ all fall within the standard deviation of 5%, the 8YSZ3000dp displays a significantly higher conductivity value above ~350 °C. The conductivity value for the 3YSZ200dp was ~0.00023 S/cm at 450 °C, whilst it was ~0.00045 S/cm for the 8YSZ3000dp. The ionic conductivity is related to the free oxygen vacancy presence in YSZ; an increase

Fig. 6 Arrhenius plot (a) and Total conductivities plot (b) of the specimens.

Table 2 Activation energy of 3YSZ and 8YSZ.

Sample code	Bulk / eV	Grain boundary / eV	AC total / eV	4-probe total / eV
3YSZ100sc	0.40 ± 0.05	0.40 ± 0.05	0.40 ± 0.02	0.40 ± 0.02
3YSZ200sc	0.35 ± 0.05	0.40 ± 0.05	0.40 ± 0.05	0.40 ± 0.05
3YSZ200dp	0.35 ± 0.05	0.40 ± 0.05	0.40 ± 0.05	0.40 ± 0.05
3YSZ300dp+a	0.35 ± 0.01	0.42 ± 0.01	0.40 ± 0.01	-
8YSZ3000dp	0.42 ± 0.01	0.50 ± 0.01	0.40 ± 0.02	-

in the free oxygen vacancies leads to increased ionic conductivity and a lower activation energy [18]. It can be seen that all of the samples displayed similar activation energies, though the 3YSZ samples had values in the range 0.35-0.42 eV whilst the 8YSZ samples exhibited very slightly larger values in the range 0.40-0.50 eV. Reduced activation energies in fine grained YSZ has been reported to be attributed to large oxygen-ion vacancy concentrations [18].

4. Conclusions

The present study, which forms an 'interim report' on work seeking to investigate the effect of grain size and yttria content on the ionic conductivity of yttria stabilized zirconia, has already achieved a number of results. First, it has demonstrated that for grain sizes in the range 100-300 nm there is very little effect on the ionic conductivity or the activation energy. A doubling of the conductivity was obtained for the 8YSZ sample compared to the 3YSZ samples, and the activation energy was slightly larger, however the grain size was also roughly an order of magnitude larger. Further work is still ongoing to demonstrate whether it was the

yttria content or grain size that is the dominating factor. HRTEM micrographs taken on the 3YSZ showed no indication of impurities or yttria segregation, however a necklace-like structure was observed in the 8YSZ. This has been observed before when nickel and alkali silicates were present as an impurity, however, no such impurities were observed in the current work. Finally, it has been demonstrated that processing route does not appear to affect the measured ionic conductivity.

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