Journal of Alloys and Compounds 480 (2009) 639–644

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Industrial precipitation of yttrium chloride and zirconyl chloride: Effect of pH on ceramic properties for yttria partially stabilised zirconia

G.A. Carter [a,b], R.D. Hart [b], M. Rowles [c], M.I. Ogden [a,*], C.E. Buckley [b]

[a] Nanochemistry Research Institute, Curtin University of Technology, PO Box U1987, Perth, Western Australia 6845, Australia
[b] Centre for Materials Research, Curtin University of Technology, PO Box U1987, Perth, Western Australia 6845, Australia
[c] Commonwealth Scientific, Industrial Research Organisation (CSIRO), Minerals Division, Clayton, Vic, Australia

ARTICLE INFO

Article history:
Received 28 November 2008
Received in revised form 22 January 2009
Accepted 1 February 2009
Available online 10 February 2009

Keywords:
Zirconia
Yttrium
Ceramics
Precipitation
Calcination

ABSTRACT

Two 3 mol% partially stabilised zirconia (P-SZ) samples suitable for the SOFC market were manufactured from solutions through to ceramics using a method similar to a known industrial process. The only difference in preparation of the two 3 mol% P-SZ samples was the pH of precipitation which was set at pH 3 or 12. Particle size measurements by dynamic light scattering were used to characterise the precipitate and the filtration rates were investigated. Five point N_2-BET was used to investigate the specific surface area before and after calcination with the response to temperature tracked. Similarly TGA/DTA investigation was used to determine the calcination point during all of these tests and it was found that both powders behaved similarly. XRD-Rietveld analysis incorporating *in situ* and *ex situ* calcination revealed that the pH 3 sample had more monoclinic phase present after calcination and sintering as a ceramic. Ceramic testing incorporating hardness (Vickers), toughness (K_{1C}), MOR, density and grain sizing was carried out, all determined that the material produced at pH 12 was superior for SOFC applications than the pH 3 sample. Further investigation using TEM-EDS revealed that the processing of the pH 3 powder had allowed a lower concentration of the yttrium which was incorporated at approximately 2 mol% instead of the required 3. ICP-OES of the after filter liquor indicated that high concentrations of yttrium (797 ppm) were found in the solution with the wash solution having 149 ppm yttrium. In contrast the pH 12 samples had 7 ppm in both the after filter liquor and wash indicating that the yttrium is bound within the matrix more completely at the higher pH.

1. Introduction

Zirconia and yttria-doped zirconia are important technological ceramic materials. As part of an on-going research program we have been investigating the fundamental chemistry of the processing of these materials, with a core focus on industrially relevant aqueous processing. Here we are using zirconyl chloride and investigating how the aqueous processing changes might affect the ceramic performance.

Previous publications by the group have highlighted differences in the aqueous processing of both un-doped and doped zirconia in the through-processing of the wet chemistry. Small Angle X-ray Scattering (SAXS) of zirconyl chloride solution speciation demonstrated changes with solution concentration and doping levels. This work found few changes were evident by increasing the solution concentration from 0.81 to 1.62 M, however a trend was noticed with increasing yttrium chloride concentration from 3 to 10 mol% [1]. Dynamic light scattering (DLS) characterising the precipitates obtained at pH 6 demonstrated that significant particle growth was observed upon doubling the concentration and enhanced particle growth was also seen upon the introduction of doping elements, in particular yttrium [1].

Further work focused on process changes found that significant differences in precipitated particle size were caused by both the pH of precipitation and the agitation level. Investigations of materials produced at pH 3 and 12, using TGA/DTA, micro-combustion and TEM EDS, found that the precipitated zirconium hydroxide had different structures, with the pH 3 sample giving results consistent with a formulation of $Zr[OH]_4$ while the pH 12 sample was consistent with $ZrO[OH]_2$ [2]. Previous work conducted on the through-processing has in the main concentrated on un-doped zirconia and demonstrated that there were differences evident in the ceramics made from zirconia produced at the different pH values [3]. Carter et al. [1–3] outline a number of authors who have similarly found the performance of zirconia dependent on the process used in its manufacture.

The major focus of this research was to facilitate the industrial processing of zirconia for Solid Oxide Fuel Cell (SOFC) applications and therefore we have focused on the through-processing and ceramic properties of a 3 mol% yttria zirconia which is commonly

---

[*] Corresponding author. Tel.: +61 8 9266 2483; fax: +61 8 9266 4699.
E-mail address: m.ogden@curtin.edu.au (M.I. Ogden).

0925-8388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2009.02.005

called 3 mol% yttria partially stabilised zirconia (3 mol% Y-PSZ). The current work follows the processing steps from precipitation through to general ceramic testing to compare the differences between ceramics obtained from powders manufactured at pH 3 with those produced at pH 12.

The engineering/physical properties of zirconia have been thoroughly reviewed [4,5]. SOFC are devices for converting hydrogen (or natural gas) and oxygen into water with a resulting generation of electrical power. The obvious difference between a SOFC and other fuel cells is that the major component in the anodes, cathodes and electrolytes are entirely or partially made from an oxide ceramic. Badwal and Foger [6] detail that SOFC electrolytes must not only have high oxygen-ion ionic conductivity but must also be stable with respect to other cell components, and have the mechanical properties such as strength, toughness, creep and thermal shock resistance. SOFC place high demands on both the materials that they are manufactured from and the manufacturing method. In addition, the components themselves are required to have good ionic/electrical properties and be able to withstand high operating temperatures while maintaining the mechanical properties required for typical life times of 40,000–50,000 h [6].

Most SOFC manufacturers/developers are using zirconia doped with yttria as the electrolyte with variations in the amount of yttria [7]. The physical characteristics of precursor powders for the manufacture of a planar SOFC have been discussed by Bellon et al. and Ahmed et al. [8,9]. Carter et al. [10] showed that the process of co-precipitation of three initially mixed chlorides, alumina chloride, yttrium chloride and zirconium chloride, can produce an oxide powder that has a homogeneous distribution of all three constituents. This homogeneity in solid solution allows for greater control of the zirconia polymorphs, leads to better processing ability in the manufacture of the parts of the SOFC, and because of a lack of concentration gradients in the finished material is likely to lead to better lifetimes.

McEvoy [11] states that the ideal solid electrolyte was identified by Nernst as zirconium oxide with a mixture of di- or trivalent substitutes in solid solution, with the 8% yttria–zirconia being preferred. 3 mol% Y-PSZ has subsequently been found to be better due to its inherent mechanical strength [12,6]. SOFC manufacturers have investigated a range of novel formulations often with other elements substituting for yttria [12–18]. Ciacchi et al. [7] supply comparative chemical, XRD phase composition, sintered density, grain size and conductivity data for five commercially produced 3 mol% Y-PSZ, providing bench mark information for any prospective commercial producer of 3 mol% Y-PSZ for SOFC applications, although no information as to how they are made are given.

2. Experimental procedures

Solution preparation, precipitation, milling and particle sizing by DLS, were carried out as reported previously [1,3], with further details contained in the Supplementary information. It is of note that precipitation was carried out in line with a local manufacturer's technology that is of a proprietary nature [10].

After milling to a particle size ranging from 15 to 42 μm the slip was spray-dried using a binder.

Sintered sample characterisation as well as *in situ* calcination studies were conducted using X-ray diffraction (XRD) with the patterns being analysed using Rietveld refinement (full experimental details are contained in the Supplementary information).

The physical testing of the 3 mol% yttria–zirconia matrix was carried out using a range of standard or well known tests, as described in the Supplementary information.

3. Results

We have previously studied the precipitation of zirconia in the absence of yttrium, and found that pH has a significant impact on the nature of the precipitate [1,2]. The conditions used here (Table 1) are based on this earlier work. It was immediately noted that with the added yttrium, the differences in particle size (Table 1) as a function of pH are much smaller than found for the pure zirconia system [2].

Table 1
Wet chemistry conditions and physical properties (PS is mean diameter by peak intensity).

pH	Concentration of starting solutions	Agitation level	PS (μm)	Filtration rate minutes	SSA ($m^2 g^{-1}$)
3	0.81	High	2.7(1)	5	197(5)
12	0.81	High	1.8(2)	7	215(3)

Fig. 1 shows the TGA/DTA trace for both the pH 3 and 12 samples. The calcination point for both samples was approximately 400 °C with a weight loss of around 43% (pH 3, 405 °C, 42.4 wt% and pH 12, 393 °C and 44.2 wt%). Once again, the change in pH is found to induce a much smaller change than found in the pure zirconia system; previously the authors reported that a marked difference exists between zirconium hydroxide precipitated at differing pH values [2]. For a non-stabilised zirconia system the maximum weight loss was 32.5 wt% assigned to a transformation of $ZrO[OH]_2$ to ZrO_2. In this case the mass loss is significantly greater for what in relative terms is a small amount of added yttrium. One explanation for this is that the additional yttrium has changed the surface charge such that less water is driven off during the drying process prior to the TGA/DTA analysis.

Fig. 2 shows the X-ray diffraction patterns for the pH 12 sample during the calcination; Fig. 3 shows the plots for the pH 3 sample. The transformation temperature differences observed between

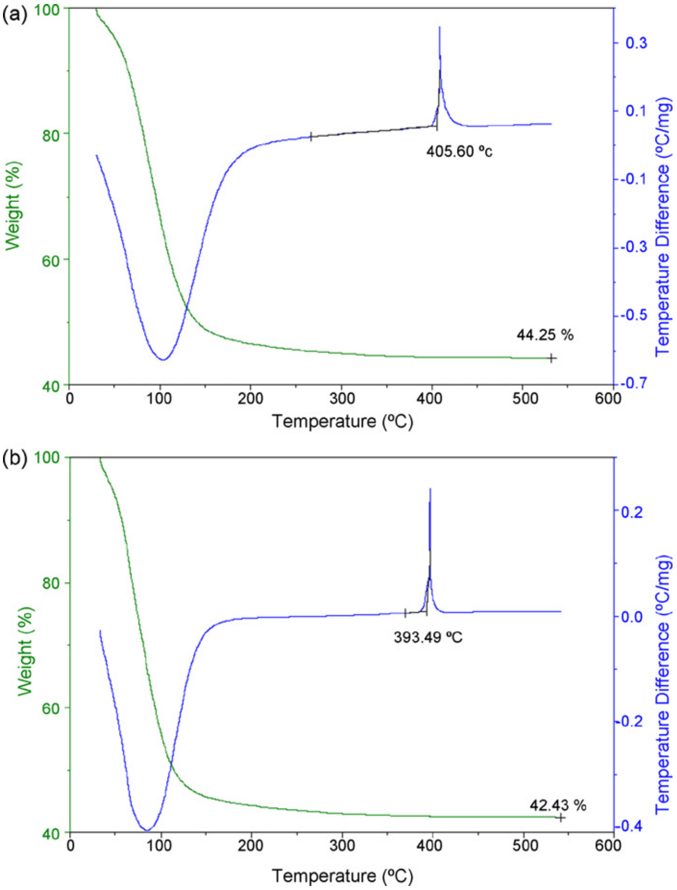

Fig. 1. TGA/DTA trace (a) pH 3 sample; (b) pH 12 sample.

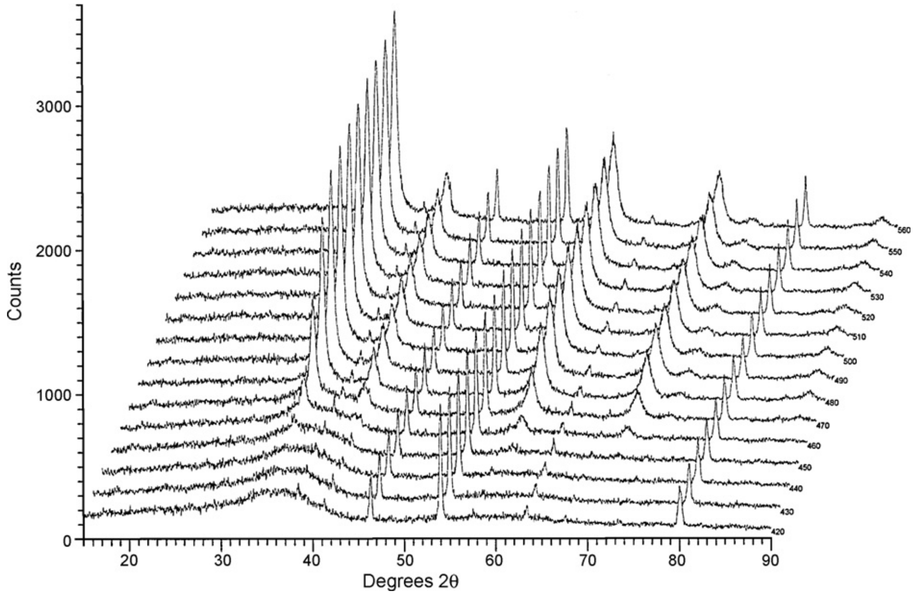

Fig. 2. XRD plots with increasing temperature through calcination, pH 12 sample.

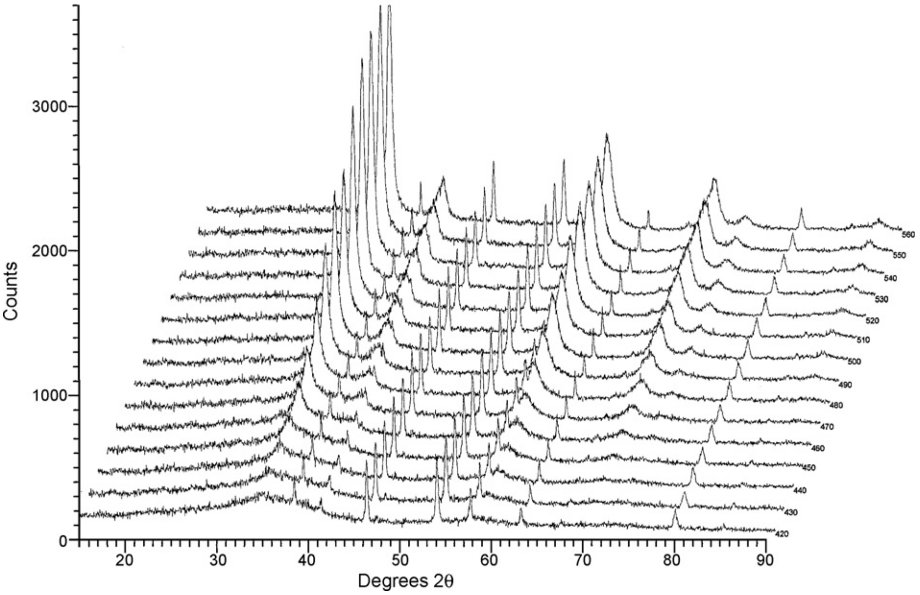

Fig. 3. XRD plots with increasing temperature through calcination, pH 3 sample.

the TGA/DTA and the X-ray diffraction are assumed to be due to experimental differences, with sample size, temperature steps with holds and temperature measuring systems all contributing. A typical pattern fit from the Rietveld analysis to determine the phase compositions of the samples with temperature is shown in Fig. 4. The results of the phase analysis are shown in Fig. 5, the phase composition % does not appear to change once the maximum tetragonal phase has been obtained. Here some differences with pH are observed; for the pH 3 precipitated samples the maximum is approximately 75%, while for the pH 12 samples it is approximately 90%.

TEM microscopy (Fig. 6) found that a crystallite size of 18 ± 5 nm within a larger aggregate was typical for both powders. The specific surface area (SSA) response with calcination was also similar, showing a linear decrease from approximately 700 °C until 1100 °C (Fig. S 3).

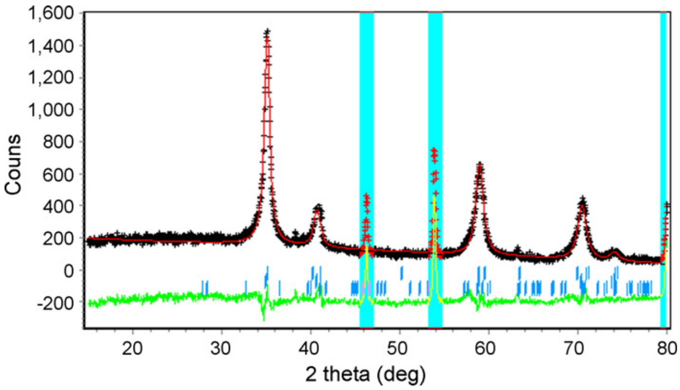

Fig. 4. Rietica plot pH 12 sample @ 580 °C (the regions of exclusion are peaks due to Pt strip heater/sample holder).

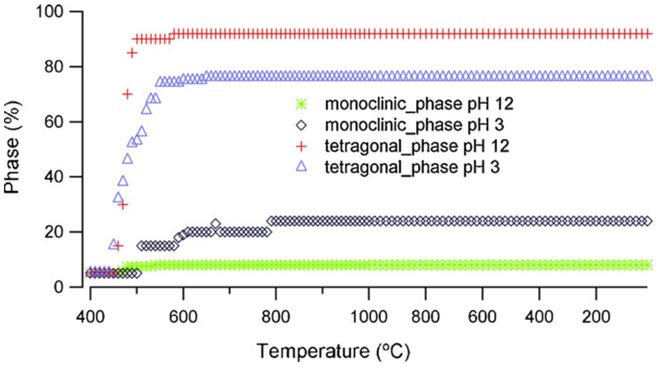

Fig. 5. Phase composition for both samples with temperature (all uncertainties for both phases are 3%).

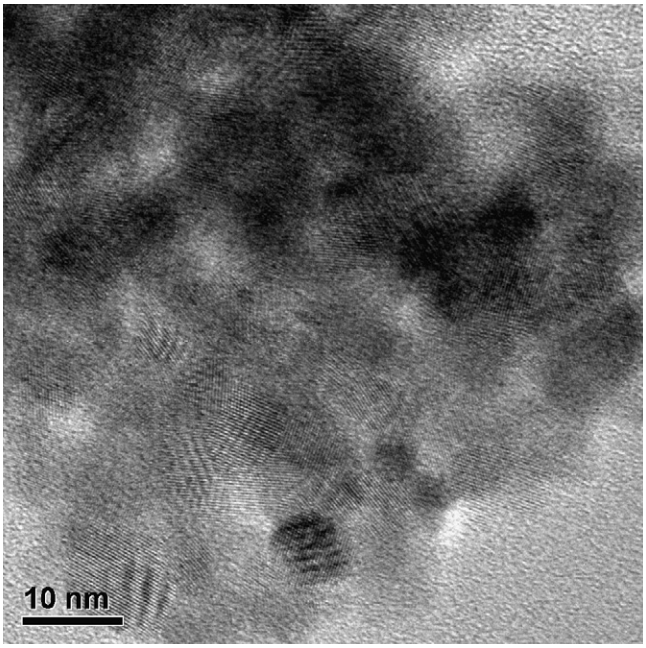

Fig. 6. pH 12 sample TEM image showing lattice planes.

Attrition milling curves for samples of powders calcined at 1000 °C were similar for the last 7 h of milling with the total time of 22 h in both cases. The responses in the first 10 h do vary, with the pH 3 sample D90 reducing more slowly than that of the pH 12, as also found for unstabilised zirconia [3]. Full milling curves are contained in the supplementary information (Figs. S 1 and 2).

The sintered density of 3 mol% Y-PSZ samples is reported to be between 6.04 and 6.08 g cm^{-3} [7,13]. Varying densities have been reported for commercial samples sintered at 4 different temperatures [14] and a similar firing regime was used here. The results (Table 2) show that the sintered densities for the pH 3 samples are between 5.88 and 5.80 g cm^{-3} with those of the pH 12 samples between 6.01 and 6.08 g cm^{-3}, depending on thermal treatment.

The density of the pH 3 sample was considerably lower than literature values, and various causes for this were considered. It has been suggested that less than optimal densities can be caused by the powder compacts containing hard agglomerates from the powder processing [15]. The strength of the spray-dried agglomerates was investigated using a literature method [16] and the powders were found to be the same (a SEM micrograph of a typical spray-dried agglomerate can be seen in Fig. S 4). Another explanation could be the porosity in the ceramic but the grain sizing micrographs showed little evidence of this (see Fig. S 5 for typical grain sizing micrograph). Investigations of the porosity of yttria–zirconia ceramics have been conducted to good effect in this manner previously [17].

Table 3
Physical properties of ceramics (fired at 1550 °C).

	pH 3	pH 12
Grain size (μm)	2(2)	2(2)
Hardness (GPa)	12.60(8)	12.46(3)
Toughness (MPa m$^{1/2}$)	6.32(9)	6.78(7)
MOR (GPa)	0.81(7)	1.02(3)
Weibull modulus	9.68	13.34

The linear shrinkage for 3 mol% Y-PSZ is reported to be 27% [18]. The values listed in Table 2 for the maximum density are slightly lower at 24 and 25% for the pH 3 and 12 samples respectively.

Table 3 shows the other physical properties obtained from the testing of the samples. The grain size of the two samples revealed that the two powders (pH 3 and 12) are similar. Grain size is linked with surface flatness of tape cast parts, with grain sizes up to 10 μm producing “excellent” flatness [8]. SEM micrographs of the powders produced here show grain sizes well below the 10 μm range. A reported generalisation is that the grain size of YSZ materials with less than 8.5 mol% yttria is usually larger than 5 μm [12]. Other reports, however, give grain sizes of approximately 0.6 μm [7,14,19]. A rather novel but simple experiment [20] showed that exaggerated growth of grains can be attributed to variation in yttria concentrations within the system, and hence the relatively small particle size distribution within the two samples in this work may indicate a relatively uniform or homogenous yttria distribution, which is an advantage of the co-precipitation method used to prepare the samples.

Hardness of the Y-SZ determined using Vickers indentation is shown in Table 3. Fig. S 6 shows a typical optical micrograph of an indentation observed in this work. The resulting values are consistent with literature [6,21,22]. Kondoh et al. [23] lists lower densities and higher hardness and toughness values for ceramics with lower yttrium levels. In Hsieh and Tuan [20] the value for the hardness and toughness for 3 mol% Y-PSZ is 13.1 ± 0.2 GPa and 4.5 ± 0.2 MPa m$^{1/2}$ for a mixture of co-precipitated 8 mol% YSZ with pure zirconia powder co-milled to form 3 mol% Y-PSZ. The increased hardness is suggested to be a result of the uneven distribution of yttria [20], the materials examined in the present work have lower hardness values but have higher toughness values. Hsieh and Tuan [20] used the K_{1C} method to determine the hardness, which is the same method employed here following literature procedures [24]. However, Kruzic and Ritchie [25] suggest that this may not be suitable due to secondary cracking which is evident in Fig. S 6. The K_{1C} method has nevertheless been used for this work as results using the method suggested by Kruzic and Rictchie [25] are rarely reported.

Table 2
Sintering temperature vs density and % linear shrinkage (uncertainties are std. deviation of 5 samples).

Sintering temperature	pH 3 density (g cm^{-3})	% Linear shrinkage	pH 12 density (g cm^{-3})	% Linear shrinkage
1650	5.85(1)	20(3)	6.04(2)	20(2)
1550	5.88(1)	24(1)	6.08(2)	25(1)
1450	5.86(2)	21(3)	6.03(2)	20(4)
1350	5.80(5)	19(2)	6.01(4)	20(3)

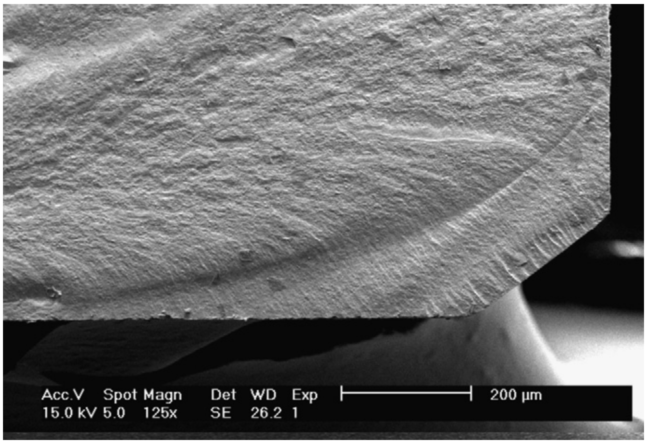

Fig. 7. MOR bar broken surface showing chamfer (pH 12).

Kondoh et al. [23] list tensile strength against the yttria content for commercially available Y-SZ and Y-PSZ. They found that the tensile strengths of 2.6, 3 and 4 mol% Y-PSZ were the same. They also found K_{1C} fracture toughness values of for the 2.6 and 3 mol% samples of 5 MPa $m^{1/2}$ and the 4 mol% had a value closer to 6 MPa $m^{1/2}$. These values are comparable with those determined here (Table 3).

A comparison of the bars manufactured for the Modulus of Rupture (MOR) test showed that their optical properties appeared to be different (Fig. S 7), although the reason for this is not apparent at this stage. The value of 1.02 GPa developed for the pH 12 sample exceeds that listed by Badwal and Foger [6]. However these authors also list 900 MPa as the lower limit, which the pH 3 sample does not reach. The minimum Weibull modulus requirement for a modern engineering ceramic is 9.7 which both samples achieved (pH 12 = 13.34, pH 3 = 9.86, Table 3) [26]. Fig. 7 is a typical micrograph of the fractured surface of the MOR bars showing there were no indications of poor forming or sintering in either sample.

Fig. 8 shows the XRD traces for the sintered ceramics of both samples, the differences are mainly the presence of higher concentrations of monoclinic phase in the pH 3 sample compared to the pH 12 sample. The hump at 28.44° 2θ in Fig. 8 is similar to the literature result for a 2.6% sample [27] suggesting the pH 3 sample may have this composition. This hypothesis was tested by TEM EDS analysis.

TEM EDS determined yttria values for the two samples were 3.3(8) wt% for pH 3 and 5.5(4) wt% for pH 12 (equivalent to 1.8 and 3 mol%; figures in brackets are the uncertainties in the last decimal place from the standard deviation of 20 sample points). The difference was unexpected as both samples were produced from the same initial solution compositions.

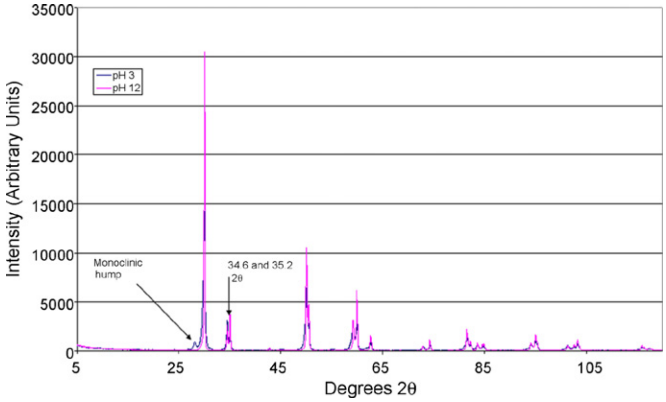

Fig. 8. XRD of the sintered ceramics.

Table 4
ICP-OES results of liquor and wash for yttrium.

Sample	Y (ppm)
pH 3 liquor	797
pH 3 wash	149
pH 12 liquor	7
pH 12 wash	7

Literature values [13] for the densities of 1.7, 2.2, 2.8 and 3.1 mol% Y-PSZ are given as 5.842, 6.044, 6.085 and 6.077 g cm^{-3} (measured). In this work, the pH 3 sample returned a density of 5.88 g cm^{-3} and the pH 12 gave 6.08 g cm^{-3}. This would suggest that the pH 3 sample had between 1.7 and 2.2 mol% yttria consistent with the TEM EDS result of 2 mol%.

Subsequent testing of the liquor after passing through the filter and of the wash solution using ICP-OES indicated that minimal yttrium is lost from the pH 12 processing, however the pH 3 sample had high levels of yttrium in the liquor as well as the wash (Table 4). This would indicate that the yttrium is not precipitating out under the acidic conditions in such a way as to be tightly bound within the zirconium matrix thus allowing it to be lost in the subsequent processing steps. This is a significant finding as the industrially relevant process that this research is based upon uses formation in the acidic region.

4. Conclusions

Two Y-PSZ powders were produced using the same initial chemical mix and the same processing with the exception of pH of precipitation, and both were processed through to ceramics. The two pH values used were 3 and 12 and throughout the processing the two samples behaved remarkably similarly. The precipitated particle sizes, filtration rate and SSA for the pH 3 sample was found to be 2.7(1) μm, 5 min and 197(5) $m^2\,g^{-1}$ while the pH 12 sample had 1.8(2) μm, 7 min and 215(3) $m^2\,g^{-1}$, both samples calcining at approximately 400 °C. *In situ* XRD used to determine the phase evolution with temperature from 350 °C through to 1000 °C and returning to room temperature which showed that the pH 3 sample obtained approximately 75% tetragonal phase while the pH 12 sample obtained 90% tetragonal phase. The total milling time for both samples was 22 h although slight differences were noted in the milling curves. The spray-dried mill slip produced a free flowing powder for both samples that when investigated using SEM and powder compaction methods showed a well formed and regular powder.

The mechanical properties of the final sintered ceramics showed differences in the results for density, hardness, toughness and MOR measurements. The pH 3 sample was harder but had lower toughness and MOR than the pH 12 sample. Differences in the XRD patterns of the final sintered ceramic were noted with the pH 3 sample having higher levels of the monoclinic phase. The similarity of the pH 3 sample to that in literature for a 2.6 mol% Y-PSZ suggested that the yttrium level was lower than expected from the starting solution concentrations. TEM-EDS investigation revealed that the pH 3 precipitated sample had 3.3(8) wt% and pH 12 = 5.5(4) wt% (≈2 and 3 mol% respectively). This difference in yttria content explains the differences in the mechanical properties with the density of the pH 3 sample matching well to the theoretical density of a powder made from 1.7 to 2.2 mol% Y-PSZ.

Subsequent testing using ICP-OES indicated that when the processing is conducted at pH 3, high levels (797 ppm) of yttrium are found in the liquor after filtering with lower levels (149 ppm) found in the wash solution after filtering. In contrast only 7 ppm was found in both the liquor and wash for the pH 12 precipitated sample. Precipitation at such low pH for Y-PSZ powders is not feasible as the loss of yttrium in the filtering and washing of precipitate adversely affects the final properties of the ceramic.

Comparisons made to products currently available in the market for use in SOFC manufacture indicate that the process used to produce the pH 12 sample would be suitable for the manufacture of SOFC.

Acknowledgements

G.C., C.B. and M.O. acknowledge the financial support of the Australian Research Council (ARC) for ARC linkage grant LP0561922. G.C. is the holder of an Australian Postgraduate Award (Industry) and AINSE Postgraduate Research Award.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jallcom.2009.02.005.

References

[1] G.A. Carter, M.I. Ogden, C.E. Buckley, C. Maitland, M. Paskevicius, Powder Technol. 188 (2009) 222.
[2] G. Carter, M. Rowles, R. Hart, M. Ogden, C. Buckley, Powder Technol. 191 (2009) 218.
[3] G. Carter, M. Rowles, R. Hart, M. Ogden, C. Buckley, Mater. Forum 32-2008 (2008) 82.
[4] R.H.J. Hannink, P.M. Kelly, B.C. Muddle, J. Am. Ceram. Soc. 83 (2000) 461.
[5] D.J. Green, R.H.J. Hannink, M.V. Swain, Transformation Toughening of Ceramics, CRC Press, Inc., Florida, 1989.
[6] S.P.S. Badwal, K. Foger, Mater. Forum 21 (1997) 187.
[7] F.T. Ciacchi, K.M. Crane, S.P.S. Badwal, Solid State Ionics 73 (1994) 1994.
[8] O. Bellon, R. Ratnaraj, D. Rodrigo, 10YSZ based electrolyte materials for electrolyte supported SOFCs, in: Presented at 5th European SOFC Forum, Proceedings, 2002.
[9] K. Ahmed, J. Love, R. Ratnaraj, High performance cell development at CFCL, in: Presented at Electrochemical Society Proceedings, 2001.
[10] G.A. Carter, R.D. Hart, N.M. Kirby, D. Milosevic, A.N. TiTkov, J. Aust. Ceram. Soc. 39 (2003) 149.
[11] A.J. McEvoy, J. Mater. Sci. 36 (2001) 1087.
[12] S.P.S. Badwal, F.T. Caicchi, Ionics 6 (2000) 1.
[13] R. Ingel, D. Lewis, J. Am. Ceram. Soc. 69 (1986) 325.
[14] S.P.S. Badwal, F.T. Ciacchi, K.M. Giampietro, Solid State Ionics 176 (2005) 169.
[15] O.C. Standard, C.C. Sorrell, Key Eng. Mater. 153–154 (1998) 251.
[16] R.L.K. Matsumoto, J. Am. Ceram. Soc. 69 (1986) C246.
[17] A.G. Mawson, G.A. Carter, R.D. Hart, N.M. Kirby, A.C. Nachmann, Mater. Forum 30 (2006) 148.
[18] S.K. Tadokoro, E.N.S. Muccillo, J. Alloys Compd. 344 (2002) 186.
[19] S.P.S. Badwal, F.T. Ciacchi, V. Zelizko, Ionics 4 (1998) 25.
[20] G.H. Hsieh, W.H. Tuan, J. Mater. Sci. Lett. 21 (2002) 391.
[21] N. Gupta, P. Mallik, B. Basu, J. Alloys Compd. 379 (2004) 228.
[22] N. Gupta, P. Mallik, M.H. Lewis, B. Basu, Euro. Ceram. Viii, Pts 1-3 vol. 264–268 (2004) 817.
[23] J. Kondoh, H. Shiota, K. Kawachi, T. Nakatani, J. Alloys Compd. 365 (2004) 253.
[24] G.R. Anstis, P. Chantikul, B.R. Lawn, D.B. Marshall, J. Am. Ceram. Soc. 64 (1981) 533.
[25] J.J. Kruzic, R.O. Ritchie, J. Am. Ceram. Soc. 86 (2003) 1433.
[26] D.R. Askeland, P.P. Phule, Essentials of Materials Science and Engineering, Thomson, Toronto, Ontario, Canada, 2004.
[27] J. Kondoh, J. Alloys Compd. 375 (2004) 270.