

Role of dispersion conditions on grindability of yttria stabilized zirconia (YSZ) powders

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Abstract. A precursor for zirconia – 8 mole% yttria (YSZ–ZrO₂–8 m% Y₂O₃) powder was prepared by coprecipitation and the calcination temperature was fixed as 900°C from TG–DTA and XRD studies. The calcined powder could be dry ground only to a mean particle size (D_{50}) of 6 µm containing substantial amount of coarse agglomerates in the size range 10–100 µm. The dispersion conditions for its wet grinding were evaluated through zeta-potential and viscosity studies. The zeta-potential variation with pH of the aqueous suspensions of the powder exhibited maximum numerical values at 3 and 11 pH, exhibiting the ideal pHs for dispersion stability through electrostatic coulombic repulsion mechanism. Slurries of dry ground powders with solid concentration in the range 15–30 vol.% exhibited pseudo-plastic flow characteristics, indicating presence of floculates. With progress of grinding, the increase in viscosity of the slurries became less significant with decreasing solid concentration. Even though the particle size of the ground slurries decreased with decreasing solid content, there was little change in it for slurries with solid content < 20 vol.%. Grinding conditions for formation of sinter-active powders of YSZ with sub-micron size ($D_{50} \sim 0.7$ µm free of agglomerates of size > 5 µm) were established. Compacts from this powder could be sintered at 1400°C to translucent bodies with 99% theoretical density.

Keywords. YSZ powder; dispersion behaviour; grindability.

1. Introduction

During the synthesis of oxide powders by solution based techniques (e.g. solution combustion, decomposition of metal nitrates, precipitation etc), agglomerates of fine crystallites of the precursors or oxides form and their size vary up to many microns. The calcination conditions for formation of the oxide from the precursor precipitates are generally fixed through detailed TG–DTA and XRD studies. Broad size distribution and presence of coarse agglomerates (size > 10 µm) in the calcined powder lead to formation of heterogeneity in green microstructure of the shapes formed by both wet casting and dry pressing techniques. Such heterogeneities introduce defects in the final sintered bodies leading to deleterious effects on their properties. Bodies could not be sintered to near theoretical density with no porosity. Grinding of these agglomerates into fine particles free of coarse ones (mean size of $D_{50} < 1$ µm) improves densification to near theoretical density at a relatively lower temperature and results in homogeneous microstructure. Thus a study of grinding behaviour of the oxide agglomerates formed during precipitation and calcination is an important aspect. The grindability of the powder is influenced by various para-

meters, e.g. powder preparation conditions (reactant concentrations, washing and drying conditions), milling conditions (mill parameters) and dispersion conditions of the powder in suspending media (water content and its pH). During dry grinding, with decrease in the agglomerate size, the powder forms a cake along the walls of the pot. Further reduction in the agglomerate size is possible only by wet grinding. Efficiency of wet grinding is influenced by the dispersion conditions used. Even though a large amount of literature is available for the synthesis of fine powders of advanced ceramic materials, no systematic study is reported about the role of dispersion conditions on the grinding behaviour of these agglomerates to fine powder and its sinterability.

The dispersion of oxide particles in water can be achieved by either the electrostatic coulombic repulsion mechanism (due to presence of adsorbed charge on them) or by steric hindrance mechanism (due to the adsorption of a polymeric molecule on their surface) (Pierre 1991). During grinding it is essential to keep both the particles being ground and formed, dispersed so that further grinding remains efficient (i.e. flocculation is expected to hinder efficiency of grinding). Flocculation occurs due to the weak Van der Waal force of attraction in the absence of charge on the particles. An underestimated aspect of study in processing of agglomerates of ceramic oxide powder is the role of dispersion conditions on their grindability. Even though it has been emphasized for the slurry formu-

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lation for shape forming by slip casting and tape casting techniques (Fries and Rand 1996; Hellobrand 1996), not much study exists on the role of dispersion on the grinding behaviour of agglomerates of oxides formed by solution based techniques.

The role of dispersion conditions on the mixing and grinding of oxide powders in aqueous media is discussed recently (Houivet *et al* 2002). The quantitative parameters used for evaluating the degree of dispersion in aqueous oxide suspensions are zeta-potential and rheological behaviour (Hunter 1981; Jean and Wang 2000; Houivet *et al* 2002). The zeta-potential is a measure of the amount of charge present on the particle surface relative to the bulk of the aqueous media so that columbic repulsion between them stabilizes their dispersion. It is a function of the powder characteristics, presence of impure ions and pH of the medium. Even at the pH of maximum zeta-potential, with increasing solid concentration in suspension (i.e. in slurries of powders), flocculates are said to exist and is exhibited by shear thinning characteristics (i.e. the pseudo-plastic flow behaviour), which is attributed to the breaking away of flocculates upon shearing (Reed 1995; Vallar *et al* 1999). Lesser viscosity and lesser dependency of it with shear rate are characteristics of a good dispersion. For effective grinding, zeta potential of the slurry should be maximum and the solid concentration should be such that the shear experienced during grinding in the mill is high enough to break the flocculates.

Highly dense yttria stabilized zirconia (YSZ) bodies find application as electrolyte materials for solid oxide fuel cells (SOFC), oxygen sensor, pumps etc (Jaganathan *et al* 1980). These components are synthesized through standard ceramic processing techniques such as slip casting, extrusion, tape casting and dry pressing. The most versatile method for preparation of the powder required for the above processes is co-precipitation technique. The co-precipitated gel decomposes into crystalline oxide compound upon heating and the conditions are generally obtained through a detailed TG-DTA and XRD studies. As emphasized previously, elimination of the coarse agglomerates present in the calcined powders into sub-micron size by wet grinding is essential for making the above-mentioned components with high density and homogeneous microstructure at a lower sintering temperature. There is no reported literature on the effect of dispersion conditions on the grindability of YSZ powder agglomerates formed by co-precipitation technique. Hence the above aspects were studied.

2. Experimental

The hydroxide gel of zirconium and yttrium (corresponding to ZrO_2 -8 m% Y_2O_3 composition) was prepared by the standard reverse strike co-precipitation by drop-wise addition of a solution of zirconium oxy-chloride and

yttrium nitrate (0.1 M metal ion concentration) into a bath of excess ammonia (0.1 M) kept stirred vigorously. The jelly precipitate formed was filtered, washed repeatedly till no trace of chloride was found by silver nitrate test. The wet gel was oven dried at 70°C. The oven dried gel was dry ground in a planetary mill (M/s Fritsch, Germany) to form into powder. This precursor powder was subjected to TG-DTA (M/s Netzsch) and XRD (M/s Philips) studies to fix the calcination temperature. The precursor was calcined at 900°C to form into the oxide compound (YSZ).

The precursor powder calcined at 900°C was dry ground planetarily for 1 h. The particle size distribution of the powder agglomerates was obtained using laser light scattering technique (Master-sizer 2000 from M/s Malvern, UK). The zeta-potential variation of the aqueous suspensions of the powder with pH was obtained by laser Doppler velocimetry (Zetasizer 3000 from M/s Malvern, UK), while the variation of viscosity with shear rate for slurries of varied solid concentrations were obtained using a cone and plate viscometer (M/s Boehlin, UK). Both the dry and wet grinding studies were carried out in the planetary mill under a standard set of conditions (30 g of powder in 80 cc alumina pot with 15 alumina balls of 10 mm diameter at a mill r.p.m. of 200). The extent of grinding was assessed through determination of their particle size distributions. Wet grinding was carried out up to 10 h. The sinterability of the powders with varying sizes has been evaluated from the bulk density of the dry pressed (150 MPa) samples sintered at 1400°C for 2 h and the sintered specimen characterized for its microstructure.

3. Results and discussion

The TG-DTA pattern of the precursor is shown in figure 1. The oven dried precursor exhibited a total loss of weight

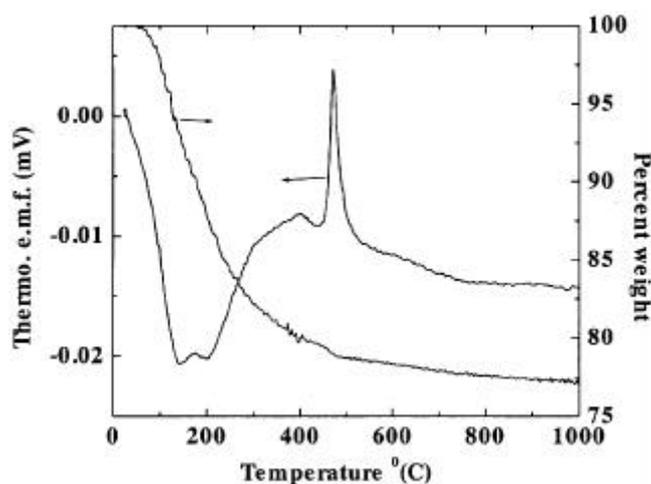


Figure 1. TG-DTA pattern for oven dried YSZ gel.

of about 24% in stages (temperature ranges, 25–300 and 400–500°C) accompanied by a broad endotherm and a sharp exotherm. The endotherm has been attributed to the loss of capillary water and water of adsorption while the exotherm is attributed to the crystallization of cubic YSZ phase (Ramanathan 1995). Even though the exotherm was complete below 500°C, there was a minor amount of loss in weight up to 900°C. Hence the gel was calcined at 900°C and was found to be cubic YSZ phase as shown by XRD (figure 2, pcpdf no. 30-1468). As the calcined powder upon dry grinding for 1 h formed a cake along the walls of the pot, dry grinding was stopped at this stage. The particle size distribution of the powder dry ground for 1 h and that subsequently wet ground are shown in figure 3. It is obvious that dry grinding yields powder

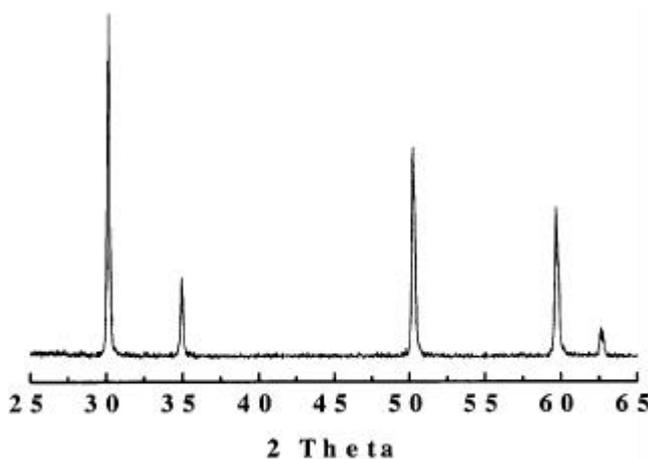


Figure 2. XRD pattern for YSZ gel calcined at 900°C.

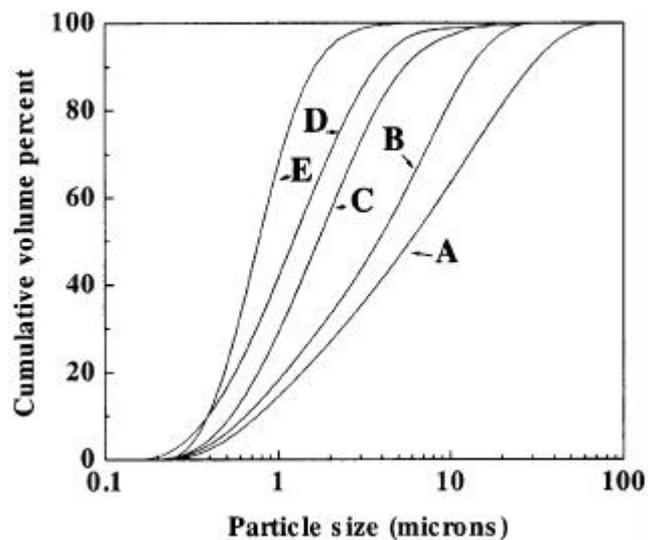


Figure 3. Particle size distribution of the dry and wet ground slurries (20 vol.% solid content at a pH of 3). A. powder dry ground for 1 h; B, C, D, E. wet ground for 1, 2, 4, 10 h, respectively.

agglomerates with their mean size of about 6 μm containing substantial amount of coarser particles (size > 10 μm) which need to be eliminated to improve their sinterability to near theoretical density. As dry grinding for 1 h resulted in formation of cake along the walls of the pot, the coarser agglomerates present at this stage can be eliminated only by wet grinding.

As discussed previously, efficient wet grinding needs well-dispersed slurries. As the degree of dispersion of the slurries is quantitatively measured through zeta-potential and rheological behaviour, these aspects were studied. The variation of zeta-potential with pH of the aqueous suspensions of the YSZ powder, as shown in figure 4, exhibited a maximum in the numerical value in the pH ranges 2–3 (positive value) and 10–11 (negative value). It is generally positive in acidic and negative in alkaline media. As the zeta-potential is characteristic of the surface composition of the material, the numerical value has been found to vary with preparation conditions (like precursor compound, calcination temperature) and the medium. There is a wide variation in the reported values of zeta-potential of the YSZ powders and is attributed to the method of preparation and trace amounts of impurities (Seabsugh *et al*; Basu *et al* 2001; Ramanathan *et al* 2004). The pH at which the net charge on the surface of the suspended particles become zero (i.e. point of zero charge) was again characteristic of the nature of the oxide compound and it was found to be at a pH of 6 for this powder. The numerical value of maximum zeta-potential was more in acidic medium than in alkaline medium (figure 4). Hence slurries of YSZ were formulated at a pH of 3.

The variation in viscosity plots for slurries with varying volume percent solid content of un-ground powder is shown in figure 5. The viscosity of the slurry with 30

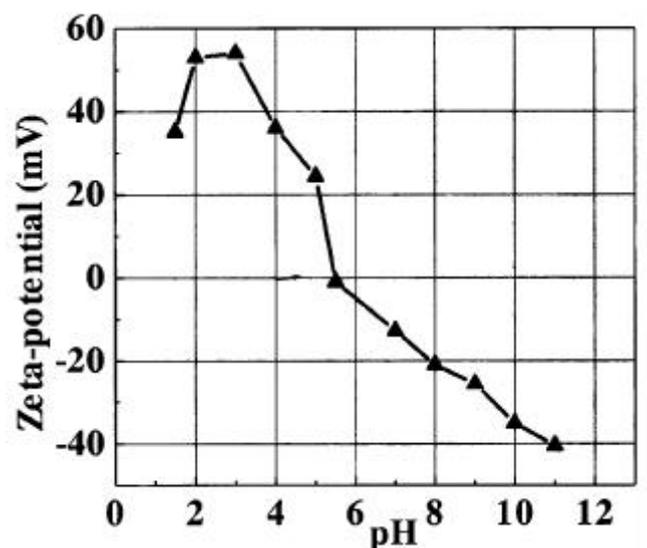


Figure 4. Zeta-potential variation with pH for aqueous suspensions of 900°C calcined YSZ powders.

vol.% solid at a pH of 6 was higher than that of the same slurry at a pH of 3, bringing out the importance of zeta-potential on the viscosity. At the point of zero charge (i.e. pH of 6), the particles in suspension does not possess any charge and hence they flocculate leading to higher viscosity. As the viscosity is lower at the pH of maximum zeta-potential, slurries were formulated at this pH. As the solid content decreased from 30–15 vol.%, the slurry viscosity and its dependence with shear rate decreased. Further, the decrease becomes less significant with decreasing solid

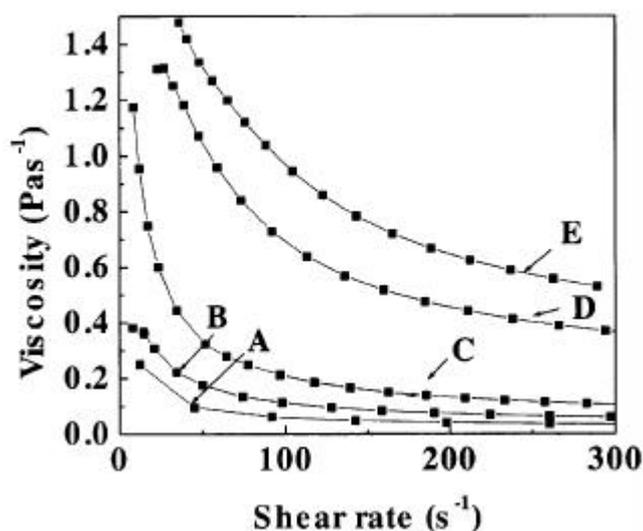


Figure 5. Variation of viscosity with shear rate plots for YSZ slurries (before grinding) A, B, C, D, slurries 15, 20, 25 and 30 vol.% solid contents at a pH of 3. E. slurry with 30 vol.% solid content at a pH of 6.

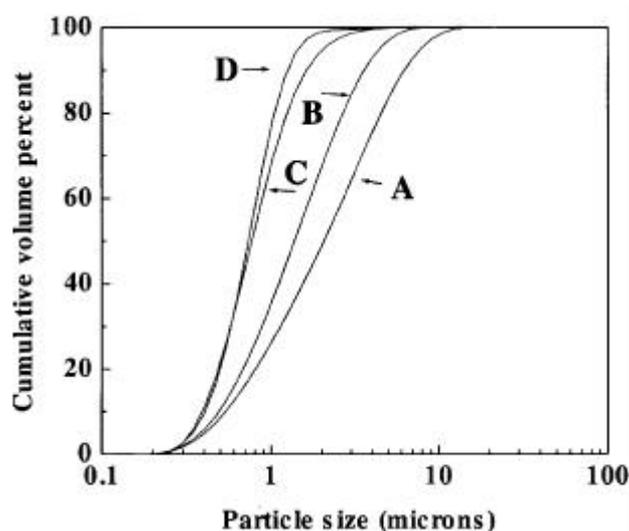


Figure 6. Particle size distribution of the wet ground slurries with varying solid contents. A, B, C, D, slurries with 30, 25, 20, 15 vol.% solid content.

content in the slurry. The shear rate above which viscosity becomes independent of it also decreases with dilution.

The flocculates present in slurries entrap water inside their structure thereby making it not available for flow and hence increase the viscosity. Upon shearing, the flocculates break and the water becomes available for flow thereby decreasing the viscosity. Thus the decrease in the viscosity with increasing shear rate has been attributed to the breaking away of the flocculates present in the slurries. The shear rate above which viscosity becomes less dependent on it (i.e. closer to Newtonian behaviour), is a measure of the strength of the flocculates. A decrease in this value with decreasing solid concentration in slurries exhibits decrease in the flocculate strength. In the shear rate independent region of the viscosity plots these flocculates cease to exist. For a given set of conditions of grinding, the shear experienced by the slurries during grinding is expected to remain constant. With dilution of the slurry, the shear experienced by it during grinding becomes higher than the critical shear for absence of flocculates, leading to improvement in the efficiency of the process.

The progress of grinding with time for the slurry with pH 3 and solid concentration of 20 vol.% is shown in figure 3. The time taken for grinding increases with decreasing particle size and formation of submicron size powder requires extensive grinding. Even though it takes only 2 h to reduce the mean size (D_{50}) from 6 to 1.8 μm , further reduction of size to 0.7 μm takes another 8 h. The role of solid concentration on the grinding behaviour of slurries is studied and the size distribution plots are shown in figure 6. The efficiency of grinding increases with decreasing solid content in the slurry (i.e. results in a lesser particle size). However, the slurries with 15 and 20 vol.% solid content were ground to the same submicron size ($D_{50} \sim 0.7 \mu\text{m}$), while those with higher vol.% solid content could not be ground to the same degree of fineness. To understand this observation, a study on the evolution of viscosity with progress of grinding for various slurries was attempted.

The variation of viscosity before and after grinding for slurries with 20, 25 and 30 vol.% solid content is shown in figure 7. Again the increase in viscosity of the slurry with progress of grinding became less pronounced with decreasing solid content (i.e. very little change in the slurry with solid content of 20 vol.%). The evolution of viscosity with progress of grinding is attributed to formation of more particles, partial evaporation of the solvent and the change of pH. The pH of YSZ slurries with varying solid content was found to remain essentially the same (2 to 3). The loss due to evaporation is expected to be same for all slurries as the pots were covered with the lids under identical conditions. Hence dilution (i.e. increasing water content) appears to make the contributions due to increased number of particles formed and evaporation less significant. As the viscosity of the slurry remained essentially the same for solid concentration of 20 vol.% and below,

the particle size distributions of them after grinding remained the same. Slurries with solid content more than 20 vol.% exhibited higher ground size due to substantial increase in viscosity with progress of grinding. Thus the

Table 1. Solid content of slurries used for grinding (10 h), final particle size and sintered density of pellets from the powder.

Volume percent solid content in slurry	Size (D_{50} , μm)	Percent theoretical density
30	2.1	87
25	1.4	93
20	0.7	99
15	0.7	99

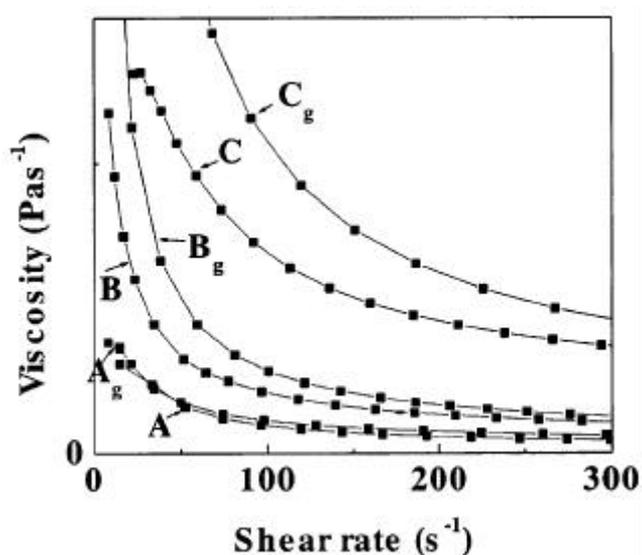


Figure 7. Variation of viscosity with shear rate for YSZ slurries with progress of grinding. A, B, C. slurries with 20, 25, 30 vol.% solid content before start of grinding; A_g, B_g, C_g. slurries with 20, 25, 30 vol.% solid content after grinding.

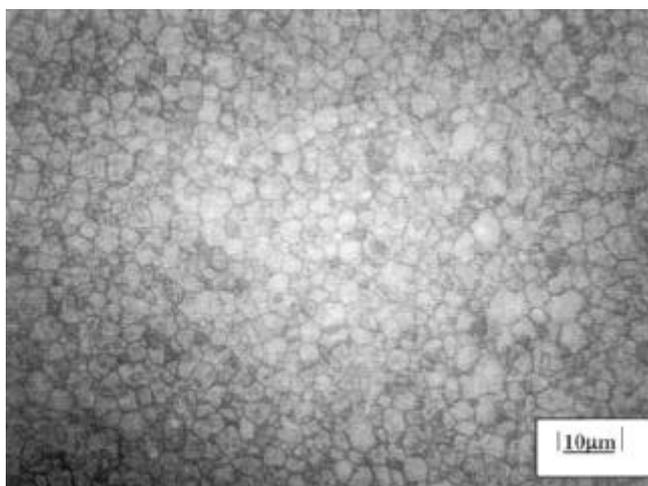


Figure 8. Typical microstructure of YSZ compact (99% T.D.) sintered at 1400°C.

increase of viscosity of the slurry during grinding appears to hamper efficiency of grinding.

The sintered density data of the compacts (sintered at 1400°C for 2 h) of powders with varying sizes (obtained by grinding with varying solid content) showed a drastic increase in the density with decreasing particle size (table 1). Translucent bodies having a density of 99% theoretical, nil open porosity and uniform grain structure (figure 8) with grain size ranging from 5 to 10 μm could be obtained at 1400°C only by using the finest powder. The contamination from the grinding media (as assessed from the weight of the balls before and after grinding) was less than 0.2%.

4. Conclusions

The oven dried YSZ co-precipitated gel crystallizes into the oxide compound below 900°C. Dry grinding yielded powders with substantial amount of coarse agglomerates (with size > 10 μm) which exhibited poorer sinterability. Only wet grinding could eliminate these agglomerates. The results of a combined study of zeta-potential, viscosity (i.e. parameters indicative of degree of dispersion) and particle size data exhibited that the slurries with solid concentration < 20 vol.% at a pH of 3 could be efficiently wet ground to form sub-micron size ($D_{50} \sim 0.7 \mu\text{m}$) powder. Bodies from this powder could be sintered at 1400°C to translucent bodies with near theoretical density.

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References

- Basu Rajendra N, Randall Clive A and Mayo Marrilea J 2001 *J. Am. Ceram. Soc.* **84** 33
- Fries Robert and Rand Brian 1996 *Materials science and technology, processing of ceramics—part I* (eds) R W Cahn *et al* (Weinheim: VCH Publishers Inc). **Vol. 17A** p. 153
- Hellobrand Hans 1996 *Materials science and technology, processing of ceramics—part I* (eds) R W Cahn *et al* (Weinheim: VCH Publishers Inc). **Vol. 17A** p. 189
- Houivet D, Fallah J E and Haussonne J M 2002 *J. Am. Ceram. Soc.* **85** 321
- Hunter R J 1981 *Zeta-potential in colloidal science – principle and applications* (London: Academic Press)
- Jaganathan K P, Tikku S K, Ray H S and Ghosh A 1980 *Technological applications of solid electrolytes and their applications* (ed) E C Subbarao (New York and London: Plenum Press) p. 201
- Jean J H and Wang H R 2000 *J. Am. Ceram. Soc.* **83** 277
- Pierre Alain C 1991 *Ceram. Bull.* **70** 1281

- Ramanathan S, Muraleedharan R V, Roy S K and Nair P K K 1995 *J. Am. Ceram. Soc.* **78** 429
- Ramanathan S, Krishnakumar K P, De P K and Banerjee S 2004 *J. Mater. Sci.* **39** 3339
- Reed J S 1995 *Principles of ceramic processing* (New York: Wiley)
- Seabsugh M M, Swartz S L and Dawson W J A Report on tubular SOFC with deposited nanoscale YSZ electrolyte (www.nextechmaterials.com)
- Vallar S, Houivet D, Fallah J E, Kervadec D and Haussome J M 1999 *J. Eur. Ceram. Soc.* **19** 1017