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Correlation between slurry rheology, green density and sintered density of tape cast yttria stabilised zirconia

Amit Mukherjee [1], B. Maiti [2], A. Das Sharma, R.N. Basu [3], H.S. Maiti *

Electroceramics Division, Central Glass and Ceramic Research Institute, Calcutta 700 032, India

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Abstract

An attempt has been made to investigate the role of dispersant and powder dimension on the slurry rheology and the corresponding effect on green as well as sintered densities of tape cast yttria stabilized zirconia (YSZ). Two commonly used dispersants, viz. menhaden fish oil (MFO) and phosphate ester (PE) have been used in conjunction with YSZ powders of different particle sizes. It has been found that for this system, PE is a much better dispersant than MFO and the best dispersion is obtained with finer YSZ powders. The slurry rheology has a marked effect on the green as well as subsequent sintered densities of the tapes. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Tape casting; A. Suspensions; E. Fuel cells, YSZ

1. Introduction

Yttria stabilized zirconia (YSZ) is the most widely used electrolyte material for oxygen sensor and fuel cell applications. Pure zirconia, ZrO_2, cannot act as a good electrolyte owing to its poor ionic conductivity and phase transformation (monoclinic/tetragonal) on heating associated with a large volume change. Doping of ZrO_2 with a small amount (3–10 mol%) of a divalent or trivalent oxide can stabilize the cubic fluorite phase and, in the process, increases its oxygen vacancy concentration leading to an enhanced ionic conductivity. This makes stabilized zirconia suitable for use as an electrolyte material and yttria (Y_2O_3) is the most commonly used dopant for stabilizing zirconia for the aforesaid applications.

The most important criterion in the fabrication of YSZ electrolyte is the production of a highly dense structure, i.e. with no connected porosity (in order to prevent cross flow of gases). Moreover, it should be as thin as possible so that the ohmic loss is minimized. Tape casting is a low cost ceramic fabrication technique that can be employed to produce wide and thin ceramic tapes having precise dimensional tolerances and very smooth surfaces [1]. It has also been observed [2] that tape casting leads to a very homogeneous microstructure. It is not surprising, therefore, that many investigators [3–6] have employed this technique to fabricate YSZ electrolyte for different applications.

In the tape casting process, ceramic powders of sufficient fineness are dispersed in a proper liquid medium followed by the addition of organic binders and plasticizers which increase the mechanical strength and flexibility of the green tapes [7,8]. However, a homogeneous product of uniform density can be obtained if the starting slurry has a high degree of homogeneity and stability. The alignments and packing of particles in the green tapes dictate the sintering characteristics and the final properties [9,10]. Hence, two basic interrelations exist: (1) between the slurry and the green tape, and (2) between the green tape and the sintered product [7]. The present work aims to study the correlation between slurry rheology, green density and sintered density of tape cast YSZ sheets.

2. Experimental

2.1. Starting materials

In order to study the effect of particle size on the slurry rheology and the latter's effect on the green and

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* Corresponding author. Fax: +91-033-473-0957.

[1] Present address: Department of Chemistry, College of Engineering and Management, Kolaghat, West Bengal, PIN 721 171 India.

[2] Present address: Department of Physics, College of Engineering and Mangement, Kolaghat, West Bengal, PIN 721 171, India.

[3] Present address: Institut für Werkstoffe und Verfahren der Energietechnik 1, Werkstoffsynthese und Herstellungsverfahren, Forschungszentrum Jülich GmbH, Leo-Brandt-Straße, D 52428, Jülich, Germany.

E-mail address: hsm@cscgcri.ren.nic.in (H.S. Maiti).

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sintered densities, fully yttria-stabilized zirconia (8 mol% yttria) from two different sources were used: TZ-8Y, Tosoh Corp., Japan (designated as T) and 8YSZ, ACC Ltd., India (designated as A). Both the powders are of very high purity (> 99.5%). The only difference is in their particle size distribution; while powder T is very fine with a median particle size of only 0.18 μm, powder A is much coarser with a median particle size of about 0.54 μm.

Suspensions of YSZ were prepared using reagent grade solvents consisting of an azeotropic mixture of methyl ethyl ketone (MEK) and ethanol (EtOH). In order to see the effect of dispersants on the slurry rheology, green as well as sintered densities of tapes, two most popular commercial dispersants [11,12] were used in the tape casting formulations: phosphate ester, PE (Emphos PS21-A, Witco Chemicals Co., New York, USA) and Menhaden fish oil, MFO (Sigma Chemical Co., St. Louis, MO, USA).

For the preparation of tape casting slurry, the binder used was a polyvinyl butyral, PVB (Butvar B 98, Monsanto, St. Louis, MO, USA) and the plasticizer was a mixture of polyethylene glycol, PEG (S.d fine Chemicals Ltd., India) and benzyl butyl phthalate, BBP (E. Merck, Germany).

2.2. Slurry preparation

The formulations of the slurries are summarised in Table 1. The powder was first milled in a solvent containing a dispersant using ZrO_2 as milling media for 12 h. This step breaks down agglomerates which may be present in the powder. In the second step, the required amounts of binder and plasticizers were added to the suspension and milled for another 24 h before final casting or rheological measurements.

2.3. Rheology

The effectiveness of different dispersants (PE and MFO) for both types of YSZ powders (T and A) was estimated from the measurement of slurry viscosity as a function of dispersant concentration. The slurry viscosities were measured using a concentric cylindrical rotational viscometer (VT 500, Haake, Germany). A range of shear rates, from 40 to 450 s^{-1} was employed.

2.4. Electrophoretic mobility measurements

For the measurement of electrophoretic mobility, suspensions containing 2 wt.% powder were prepared by ball milling the powder together with a solvent and a dispersant using ZrO_2 milling media for 4 h. The suspensions were centrifuged and the dilute supernatant suspensions containing a small number of particles were collected. These supernatant suspensions were taken in a microelectrophoresis cell (Zetameter 3.0, Zetameter Inc., USA) to note the mobility values by observing the rate of movement of the individual particles under a specific electric field using a microscope attached with the instrument.

2.5. Tape casting

Prior to casting, the slurries were vacuum deaired under constant stirring for about 2 min. This removes any entrapped air in the slurry during ball milling stage. The casting was performed using a laboratory model tape casting unit (Model 164, Incetek USA). The slurries were cast on tempered glass plates through a Doctor blade. The cast slurries were allowed to dry overnight at room temperature before they were removed from the glass plate.

2.6. Density measurements

For green density measurements, dried tapes containing plasticizer, binder, dispersant and the ceramic powder were punched into small discs of diameter 25–50 mm followed by careful measurements of their thickness. The green density of the tapes was then calculated from the weight to volume ratio.

In order to measure the sintered density of the tapes, the above mentioned pieces of green tapes were fired in air at different temperatures ranging from 1450 to 1650°C for 4 h. Both heating and cooling rates were

Table 1
Formulation particulars

Powder	Median diameter (μm)	Surface area m^2/g	I:O ratio (α)[a]	L[b]	Dispersant		Binder (β)[c]	ΣPlasticizer[d]* w.r.t binder
					MFO	PE		
A	0.54	7.43	81%	39%	–	0–2%	9.32%	136%
A	0.54	7.43	81%	51%	0–2.5%	0–2%	9.32%	136%
T	0.18	15.70	81%	45%	0–2.5%	0–2%	9.32%	136%

[a] (α) Denotes the inorganic to (inorganic + organic) ratio, i.e. wt. of ZrO_2/(wt. of ZrO_2 + dispersant + binder + plasticizer).

[b] (L) Denotes the powder loading, i.e. wt. of ZrO_2/(wt. of ZrO_2 + solvent + dispersant + binder + plasticizer).

[c] (β) Denotes the wt.% of binder with respect to wt. of the powder.

[d] (*) The wt. ratio of BBP : binder was kept at 0.26; whereas, the wt. ratio of PEG : binder was maintained at 1.10 respectively.

controlled very carefully in order to avoid warpage or cracking of the sintered tapes. The densities of the sintered discs were then measured by Archimedes' method using water as a medium.

2.7. Microstructural studies

The microstructures of the green as well as the sintered tapes were observed using a scanning electron microscope (Model 30i, Leo, UK). In order to observe the microstructure of green tapes, small pieces of the samples were exposed to solvent vapours at room temperature for 15–30 s to get etched surfaces, which were then observed under the microscope. For sintered samples, after polishing, the surfaces were etched using a mixture of 5% HF and 20% HCl (1:5 v/o) for 30–60 s. The etched surfaces were then observed under the microscope to see the microstructures.

3. Results and discussions

3.1. Effect of dispersant on the slurry rheology

We have selected two dispersants, namely, MFO and PE and their effectiveness in dispersing powder A with I:O ratio of 81% is shown in Fig. 1. It is observed from the figure that the viscosity of the tape casting slurry shows a minimum for both the dispersants at a particular dispersant concentration beyond which, the slurry viscosity increases again. However, the amount of PE (about 1 wt.%) required to reach the minimal point is half of that required for MFO (about 2 wt.%). It is also evident from Fig. 1 that the viscosity minimum is much lower and the change much sharper for the slurries containing PE as the dispersant than those containing MFO indicating the former to be a better dispersant. These observations can be explained by considering the mode of action of the two dispersants.

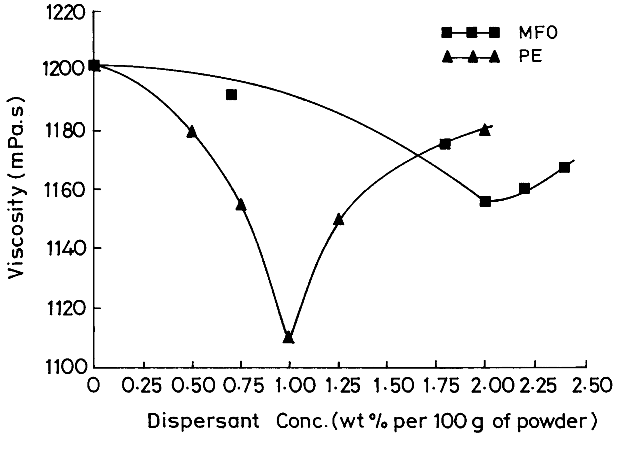

Fig. 1. Variation of slurry viscosity with dispersant concentration for different dispersants.

It is well known that the dispersion capability of MFO, which is a polyunsaturated ester molecule, is mainly due to steric stabilisation [13,14]. It has been shown [15] that during the ball milling stage breakdown of large, porous hard agglomerates takes place. These agglomerates tend to occlude liquid in the interparticle pore channels resulting in a lower quantity of solvent to flow. However, upon breakdown of these hard agglomerates to primary particles, more solvent is effectively free to flow resulting in lower viscosity. The role of a dispersant is to keep these primary particles separated from each other thereby preventing their agglomeration due to van der Waals attraction energy. It is evident from Fig. 1 that MFO is most effective to maintain the separation of these particles at a concentration of about 2 g per 100 g of powder resulting in viscosity minimum at that concentration. The increase in viscosity over the optimum dispersant concentration using MFO has been observed for other systems also [11,13].

PE (reaction product of phosphoric acid and ethoxylate; ethoxylate molecules contains both a hydrophilic polyoxyethlene group and lipophillic alkyl group) on the other hand, operates by the electrosteric stabilisation mode [7]. It has been proposed [7,16] that in a polar medium like MEK:EtOH, the decrease in viscosity below the optimum concentration of PE may be attributed to the ionization of PE on the particle surfaces to create charged surfaces leading to an electrostatic barrier. At the same time, the linear carbon chain extends into the polar solvent to provide steric stabilisation. It is believed [7] that for highly concentrated suspensions, using dispersants which shows such a combination of both electrostatic and steric mechanisms, the suspension stability will be much more compared to that where only either of the mechanisms operates. It is expected therefore, that the drop in the viscosity of the tape casting slurry utilising PE will be significantly higher than that of MFO containing slurry. However, beyond the optimum concentration, the ionized PE molecules has a tendency to interact with each other [11] so that bridging flocculation occurs [17] and the slurry viscosity increases sharply. A similar trend in the increase in viscosity of slurries beyond the optimum concentration of PE has also been observed for $BaTiO_3$ based slurries [18].

It is well established that the pseudoplasticity of a slurry is dependent on the capability of the particles to align them with increasing shear rates. With increasing particle orientation the resistance to shear decreases, thereby decreasing viscosity [19]. The shear thinning behaviour may also be due to particle flocculation [20,21]. Therefore, it is expected that the pseudoplastic effect will be lowered when there is low particle flocculation or when the particle orientation is less in the tape casting slurry. Fig. 2 represents the shear thinning behaviour of the tape casting slurries corresponding to two different dispersants (PE and MFO) in the formulations

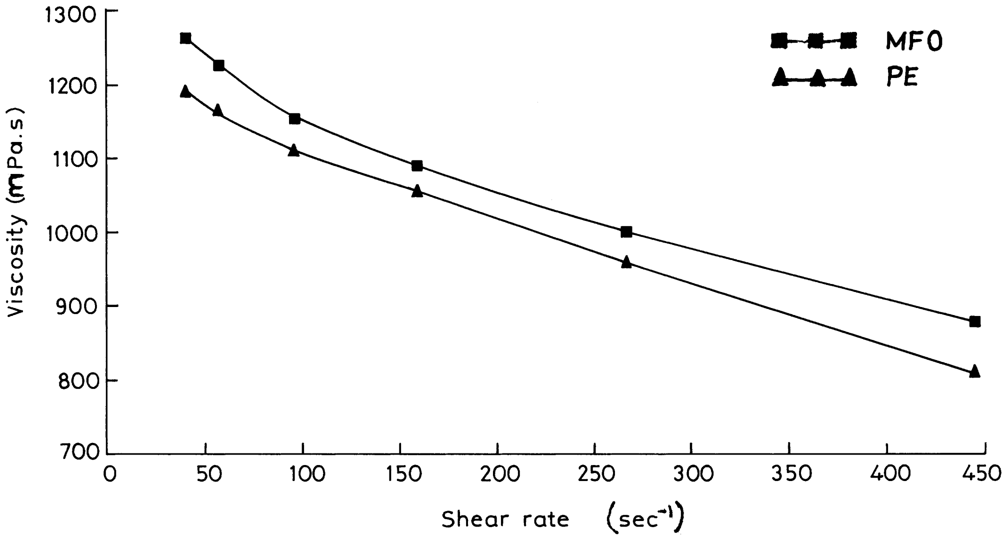

Fig. 2. Viscosity vs. shear rate plots of YSZ slurries stabilized with different dispersants.

utilising powder A. It should be mentioned here that these measurements were carried out at the optimum dispersion conditions (2 wt.% of MFO and 1 wt.% of PE in the corresponding formulations respectively). It can be observed from the plot that the viscosity of the slurries utilising MFO is higher than that corresponding to PE throughout the range of shear rates investigated (40 to 450 s^{-1}).

The shear thinning behaviour of the slurries can be monitored by an estimation of the flow index as obtained from the following empirical power law equation [22]:

$$\tau = K\gamma^n \qquad (1)$$

where τ is the shear stress, γ is the shear rate, K, a consistency factor and n is the pseduplasticity index respectively. For pseudoplastic suspensions, the value of n is less than 1 and, the greater the divergence from Newtonian behaviour, the lower is its value.

Table 2 shows the values of the pseudoplasticity index of the above two slurries calculated by Patton's method [23]. The values of n clearly demonstrate that with the increase in shear rate, the pseudoplasticity of both the slurries increases (n decreases). It is obvious from Eq. (1) that to maintain a constant change in shear rate, the change in shear stress will be lower at correspondingly higher shear rates. This would naturally imply that the value of n should decrease at high shear rates, as is observed with all the slurries investigated.

It can also be seen from Table 2 that the total change in the value of $n(\Delta n)$ for the slurry containing PE (A-PE) is greater than that of the slurry containing MFO (A-MFO). For highly concentrated suspensions of tape casting process, it is expected that even after using proper dispersants in optimum concentrations, the slurries should have agglomerated particles. Under shear conditions, as a first step, the agglomerates will be broken down into smaller units or as a terminal case to primary particles. These smaller units and individual particles will then subsequently try to orient themselves under shear. As discussed previously, the effectiveness of MFO as a dispersant is less compared to PE which results in a

Table 2
Rheological parameters for the different tape-casting slurries

Powder system	Loading (L)[a]	Torque (N.Cm)	Shear stress (Pa)	Shear rate (s^{-1})	Pseudoplasticity index (n)
A/PE	39	0.12	30.36	40.32	
		0.17	43.01	57.41	0.97
		0.27	68.31	95.94	0.94
		0.44	111.32	159.80	0.94
		0.70	177.10	266.70	0.90
		1.06	268.18	444.60	0.81
A/PE	51	0.19	47.98	40.32	
		0.26	66.88	57.41	0.94
		0.42	106.49	95.94	0.90
		0.66	168.59	159.80	0.90
		1.01	256.03	266.80	0.81
		1.42	360.12	444.60	0.66
A/MFO	51	0.20	51.00	40.32	
		0.28	70.44	57.41	0.91
		0.44	110.81	95.94	0.88
		0.68	174.18	159.80	0.88
		1.05	267.23	266.70	0.83
		1.54	391.25	444.60	0.74
T/PE	45	0.24	60.88	40.32	
		0.33	84.39	57.41	0.92
		0.51	130.47	95.94	0.85
		0.75	190.16	159.80	0.85
		1.10	280.14	266.70	0.71
		1.54	409.12	444.60	0.65

[a] L denotes the powder loading in wt.% percent.

greater degree of agglomeration in A-MFO slurry. Thus, the corresponding resistance of these agglomerates to orient them under shear will be greater. This would automatically imply that pseudoplasticity of MFO slurries will be lower compared to that of PE slurries. The above contention is reflected in the total changes of the flow index value, Δn, which may be as low as 0.17 for MFO containing slurries and as high as 0.28 for PE containing slurries.

3.2. *Effect of particle size*

The same kind of measurements on slurry rheology (viscosity, pseudoplasticity) were carried out with PE as a dispersant, but taking two kinds of powder — powder T of smaller particle size and, powder A of coarser one.

Fig. 3 shows a comparison of the viscosities of the slurries containing powder A and T as a function of PE concentration. It is evident from the figure that the viscosity of the slurry containing powder T is higher than that containing powder A throughout the range of dispersant concentration used. Similar viscosity dependence upon particle size has also been observed by several workers [24,25]. Although such higher viscosities in combination with shear thinning behaviour (discussed later) is generally attributed to flocculation of particles, electrophoretic mobility measurements show the finer particles (powder T) to have almost threefold higher mobility (1.603 $m^2 V^{-1} s^{-1}$) compared to coarser particles (powder A) for which the mobility value is only 0.495 $m^2 V^{-1} s^{-1}$. This would imply that the finer particles are better dispersed in the tape casting slurry. Thus, in order to explain such high viscosities for finer particles other factors, such as Brownian motion and electroviscous effect, should be operational in these slurries. These two phenomena are known to become increasingly important with decreasing particle dimensions [25]. These effects will be discussed briefly while comparing the pseudoplasticity effect of these slurries.

It can also be seen from Fig. 3 that the optimum dispersant concentration for the viscosity minimum for powder T is higher by around 25%. This is expected as with the decrease in particle size there is an increase in surface area of the powders in the composition. This would imply a higher amount of dispersant required to cover the surface area for effective particle separation [9,26].

The change in particle dimension also shows a reflection on the shear thinning behaviour of the slurries (Fig. 4). It is evident from Fig. 4 that the nature of the viscosity plot with shear rate for powder T differs widely from that of powder A. As a rough estimation, the ratio between the terminal viscosities for powder T is 1.71 whereas for the powder A the corresponding value is only around 1.47. Such higher changes in viscosity with shear for finer particles has been observed for other systems too [27–32] and the results indicate that the shear thinning behaviour of finer particles is a combination of the phenomena of Brownian motion and electroviscous effect [28–32]. The electroviscous effect becomes increasingly important with higher electrophoretic mobility, higher surface charge density and decrease in particle size respectively.

The flow index value (n) for the system T/PE, compared with the same for A/PE, (Table 2) also shows that the slurry corresponding to T/PE is more pseudoplastic. However, the total change in the flow index for T/PE is almost the same when compared to A/PE ($\Delta n = 0.28$). Apparently, these results may appear to be contradictory. However, considering the powder loading to be much lower in the case of T/PE slurry, the total change in the flow index is relatively higher compared to that of A/PE slurry. The powder loading was deliberately kept low in the case of powder T so as to keep its viscosity

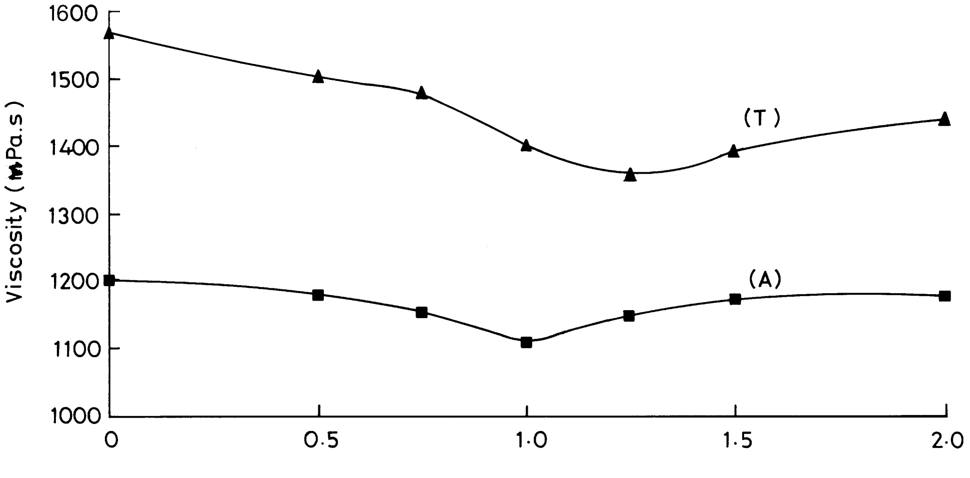

Fig. 3. Viscosities of YSZ slurries as a function of PE concentration for different powders.

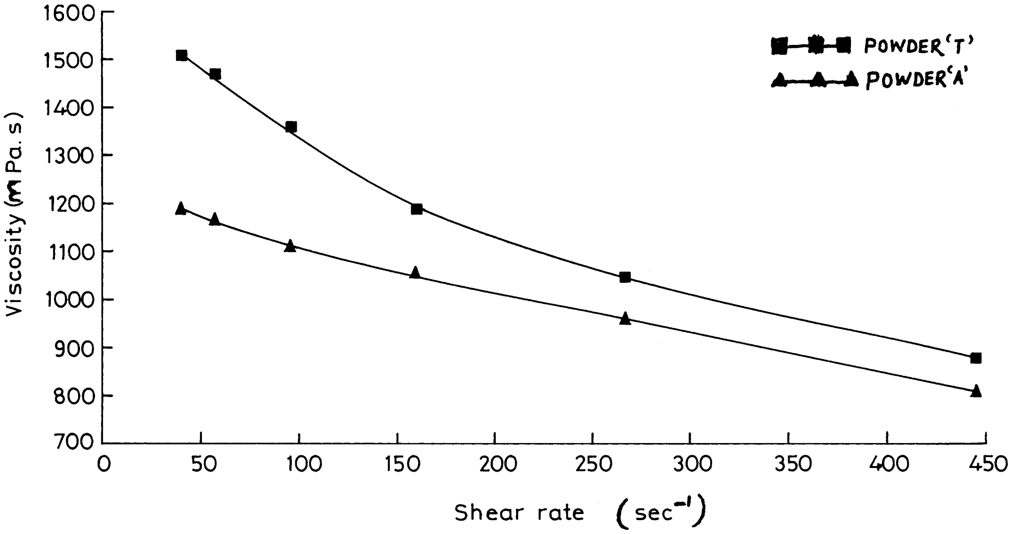

Fig. 4. Viscosity vs. shear rate plots of slurries prepared with YSZ powders of different particle sizes.

within manageable limits for the casting operation. It is evident, therefore, that in the case of fine powders, several factors have a contribution in determining the slurry rheology as discussed above.

3.3. Green density of tapes

It is well known that the state of dispersion has an important influence on the green microstructure, which develops during powder consolidation upon evaporation of the solvent. Well-dispersed suspensions tend to produce highly dense, homogeneous compacts. Figs. 5, 6 and 7 show the variation of green density as a function of the dispersant concentration. While Figs. 5 and 6 is the comparison of the changes that occur while substituting PE by MFO in the tape casting slurry; Figs. 6 and 7 show such variation by replacing powder A with powder T. It is worth mentioning that all the results reported here are taken over a large number of samples involving five different batches.

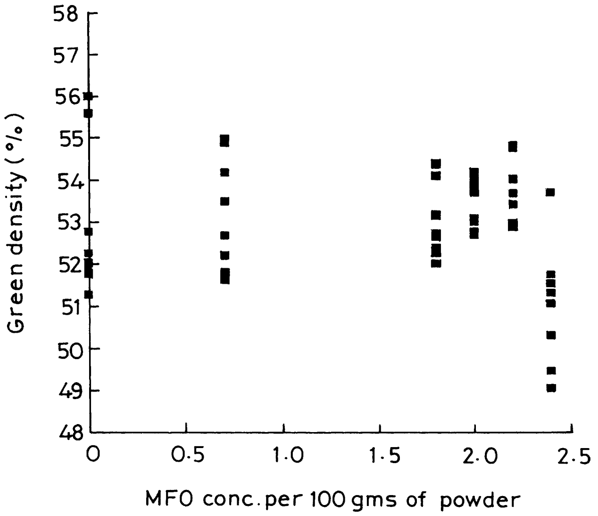

Fig. 5. Density of green tapes as a function of MFO concentration in the corresponding slurry prepared with powder A.

It is evident from Fig. 5 that with variation in MFO concentration, the mean values of green density do not change appreciably (~53% of theoretical value). However, it is more significant to note the values of standard deviation (being an index to measure the uniformity of the tapes) of these green densities with changes in MFO concentration. It is observed from Fig. 5 that the slurry corresponding to a MFO concentration of 2 wt.% per 100 g of powder is more homogeneous (as reflected from the standard deviation values) compared to other green compacts. Such variation in green density is in line with the viscosity measurements which showed that at this concentration of dispersant the degree of agglomeration is lowest.

A somewhat different trend is obtained for the slurry containing PE (Fig. 6). In this case, with changes in the dispersant concentration the mean grain density shows a gradual rise from a value of ~53% (of theoretical value) at zero dispersant concentration to a value of ~56% at a dispersant concentration of 1 wt.%. Further increase in dispersion concentration showed a negative effect on the green density. Fig. 6 also shows that the standard deviation values are lower compared to those for the MFO containing slurries, with a minimum occurring at 1 wt.% of ester. Thus, these results reflects similar trends as obtained from the rheological measurements which showed PE to be a more effective dispersant compared to MFO both in terms of maintaining particle separation and its low requirement in the slurry.

A similar trend is also observed while changing the powder dimension from A to the finer variety T with PE as a dispersant. However, in this case, the mean green

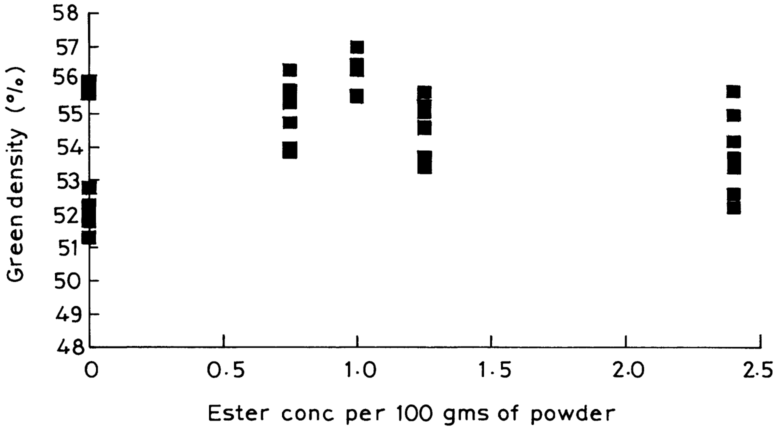

Fig. 6. Density of green tapes as a function of PE concentration in the corresponding slurry prepared with powder A.

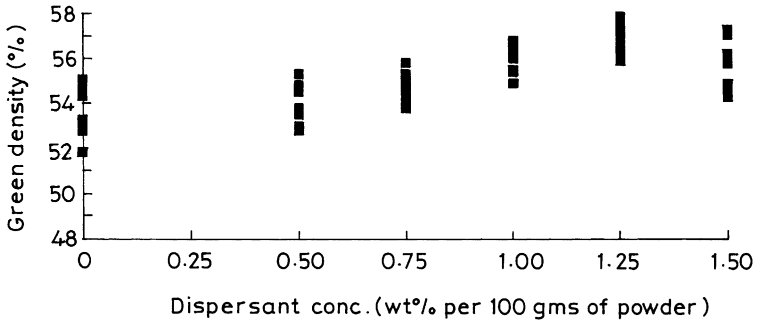

Fig. 7. Density of green tapes as a function of PE concentration in the corresponding slurry prepared with powder T.

density reaches a maximum (~57% of theoretical value) at a dispersant concentration of 1.25 wt.% (Fig. 7). Also the standard deviation of these compacts are appreciably lower compared to the deviation observed with powder A. These observations are in line with the electrophoretic mobility and rheological measurements which showed that powder T produces a more stable suspension compared to powder A under identical conditions.

Fig. 8 shows a representative micrograph of the green tape as obtained from T-PE system. However, by trying to view the microstructure of as obtained green tapes nothing significant was observed. This is primarily due to the binder phase at the surface. However, when these tapes are solvent etched selectively at the surface it opens up windows to view the microstructure of the underlying powders (Fig. 8a). A magnified look through the etched portion shows the particles are almost homogeneously distributed implying a high packing density with intermittent fine pores (Fig. 8b).

3.4. Sintering of tapes

Table 3 shows the shrinkage vis-a-vis the sintered density for the tapes obtained from the formulations representing the optimum dispersion conditions. It is observed that the trend in shrinkage is parallel to the densification process and follows the trend T-PE > A-PE > A-MFO.

It is well known [33], that the differences in the green microstructures have a profound effect on subsequent sintering behaviour; a highly ordered compact sinters to near theoretical density, whereas for suspensions involving flocs, under similar conditions of sintering, the resultant sintered density has a much lower value. Such differences in sintering are primarily due to the fact that for flocculated systems only local densification (of tightly packed particle clusters) occurs, whereas for ordered compacts, due to a large number of nearest neighbour contacts per particle and uniform small pore size, sintering is enhanced. Moreover, rearrangement and differential microdensification processes, which produce larger pores and lower shrinkage rates are minimized in ordered compacts [34]. Representative microstructures of the sintered tapes of A-PE and T-PE are shown in Fig. 9. Both the samples show existence of pores although, as expected, the porosity of the sintered substrates corresponding to powder T (Fig. 9a) is appreciably lower compared to that of the substrates prepared with powder A (Fig. 9b). Moreover, as expected [35], the sintering temperature of the fine particles are appreciably lower (1500°C) compared to that of powder A (1650°C).

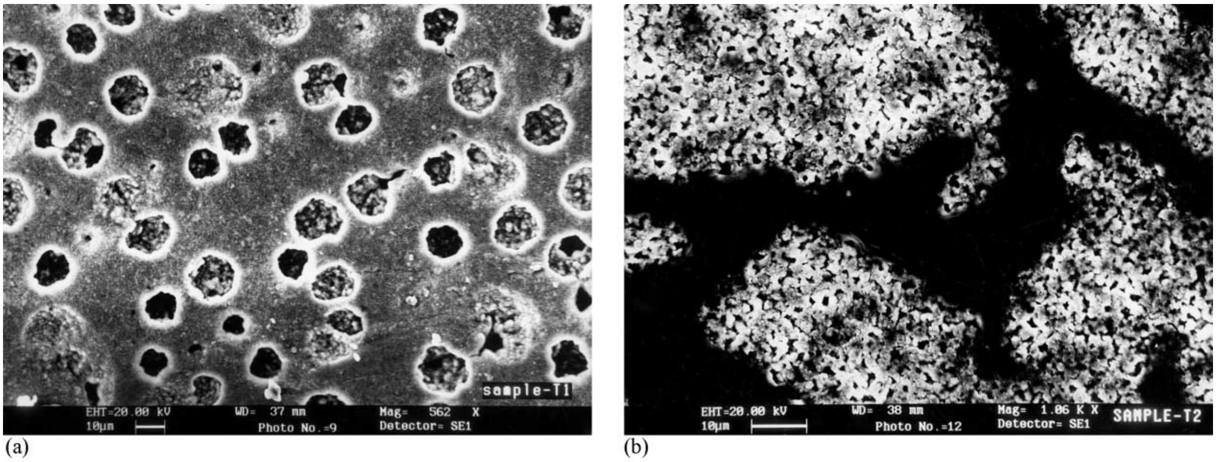

Fig. 8. Scanning electron micrograph of green tapes. (a) Solvent etched surface and (b) magnified view of the same.

Table 3
Shrinkage and sintered density of YSZ tapes

System (sintering temperature)	Comparative state of dispersion	Degree of agglomeration	Green density (% theoretical)	Shrinkage (%)	Sintered density (% theoretical)
T-PE (1500°C)	Best	Lowest	57	27	96
A-PE (1650°C)	Better	Higher	56	30	94
A-MFO (1650°C)	Poor	Highest	53	32	91

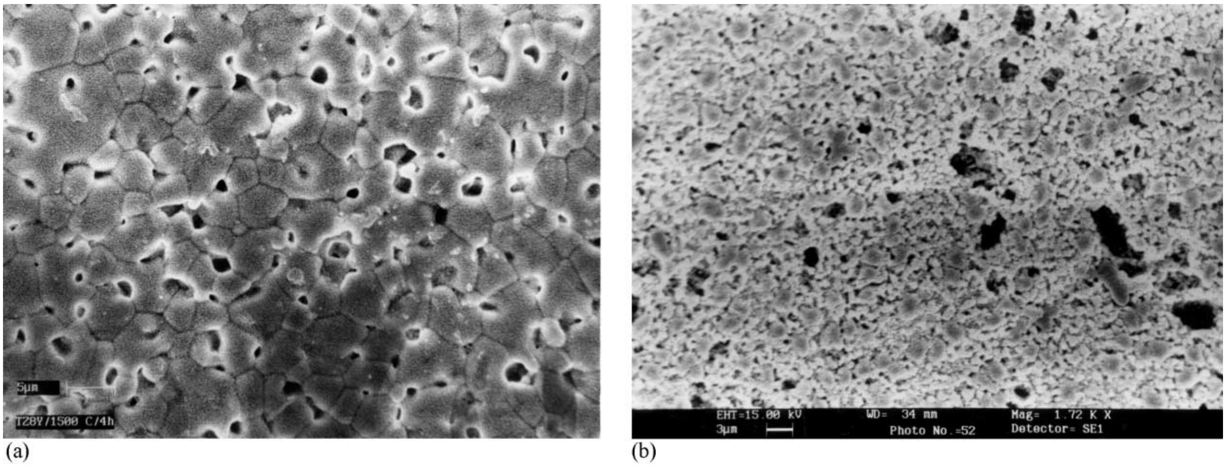

Fig. 9. Scanning electron micrograph of sintered tapes. (a) Prepared with powder T and (b) prepared with powder A.

4. Conclusions

Detailed investigations were carried out to find out the effect of the dispersant and powder dimension on the slurry rheology and the corresponding effect on green as well as sintered densities of cast YSZ tapes. The results of these experiments have revealed that in the present case, phosphate ester is a much more effective dispersant compared to menhaden fish oil as manifested in the corresponding viscosity and flow index values for the suspensions of the powders investigated. Moreover, the results point out that the degree of agglomeration is higher for slurries involving MFO, and the best dispersion was obtained with finer powders in conjunction with PE as the dispersant. It has been shown that the suspension rheology has also a profound effect on the green density and the subsequent sintered density of the tapes.

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