

Tape Casting of Zirconia for Ion Conducting Membranes: A Study of Dispersants

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(Received 6 September 1993; revised version received 22 December 1993; accepted 6 January 1994)

Abstract

Powders of fully yttria stabilized zirconium oxide have been studied in order to identify efficient dispersants for zirconia in tape casting slurries, and to verify that they do not impair the oxygen ion conductivity of the final membrane. Of eleven screened dispersants, only three were shown to be efficient. Sintered plates prepared with these dispersants had high and about equal oxygen ion conductivity ($0.16\text{--}0.19\text{ S cm}^{-1}$ at 1000°C). The use of a phosphate ester as dispersant, possibly leaving traces of phosphorus in the sintered plate, did not impair the oxygen ion conductivity. Fish oils, common dispersants for tape casting slurries, were not efficient for zirconia in the solvent system that was studied. The addition of binder and plasticizers to the dispersions to form tape casting slurries did not cause reagglomeration.

Um geeignete Dispergiermittel für das Foliengießen von Zirkondioxid zu finden, wurde vollständig stabilisiertes $\text{Y}_2\text{O}_3\text{--ZrO}_2$ -Mikropulver untersucht. Dabei galt es zu verifizieren, daß die Dispergiermittel nicht die Ionenleitfähigkeit in der fertigen Membran verringern. Von elf untersuchten Dispergiermitteln waren nur drei geeignet. Mit Hilfe dieser Dispergiermittel hergestellte gesinterte Platten zeigten eine hohe Ionenleitfähigkeit ($0.16\text{--}0.19\text{ S cm}^{-1}$ bei 1000°C). Durch die Verwendung eines Phosphorsäureesters als Dispergiermittel, das eventuell Spuren von Phosphor in der gesinterten Platte hinterläßt,

wurde die Ionenleitfähigkeit nicht beeinträchtigt. Fischöle, die gewöhnlich als Dispergiermittel für das Foliengießen dienen, erwiesen sich im untersuchten Lösungsmittelsystem als ungeeignete Dispergiermittel für Zirkondioxid. Der Zusatz von Bindern und Plastifizierern zu den Dispersionen bei der Herstellung des Schlickers führte nicht zur Reagglomeration.

L'efficacité de onze dispersants a été testée sur des suspensions de coulage en bande de zircone stabilisée (8 mol% Y_2O_3) en vue de la fabrication de membranes à haute conductivité ionique. L'étude a été focalisée sur les trois dispersants les plus efficaces. La conductivité ionique des substrats préparés avec ces trois dispersants est élevée ($0.16\text{--}0.19\text{ S cm}^{-1}$ à 1000°C). L'utilisation de dispersants de type ester phosphatique ne décroît pas la conductivité ionique malgré la présence de traces de phosphore résiduel dans le matériau fritté. Les huiles de poisson, dispersants généralement utilisés dans les suspensions de coulage en bande, présentent une très faible efficacité dans le système étudié. L'ajout du liant et du plastifiant ne perturbe pas l'état de dispersion de la suspension.

1 Introduction

Fully yttria stabilized zirconium oxide (Y-FSZ) is a common electrolyte material for use in fuel cells,

oxygen pumps and sensors. These electrochemical devices are based on selective oxygen ion transport through ion-conducting membranes. Y-FSZ is an alloy of yttria (Y_2O_3) and zirconia (ZrO_2), where zirconia is the major component (90–94 mol%). Due to the stabilizing effect of yttria, the material retains the cubic structure of zirconia at both high and low temperatures. The presence of impurities can have a marked effect on the oxygen ion conductivity in Y-FSZ.¹ For instance, silicon tends to segregate at grain boundaries forming silicates which increase the overall bulk resistance.² Due to the need of high purity materials, the whole manufacturing process to produce the membranes must be tailored with respect to contamination. For instance, ultrasonic dispersion may be less contaminating than ball milling. Another source of contamination which has to be taken into account is the organic additives used in the processing. These organics may contain elements which cannot be removed during burning-out (e.g. dispersants containing phosphorus).

Tape casting is the predominant ceramic processing technique to produce wide and thin ceramic sheets with smooth surfaces and precise dimensional tolerances.³ Moreover, it has been shown⁴ that tape casting leads to very homogeneous microstructures. Ceramic slurries for tape casting are composed of numerous components: ceramic powders, solvents, dispersants, binders and plasticizers, and other additives such as homogenizers and release agents.^{5,6} The most important factors determining the properties of the tape cast product are: (i) the properties of the ceramic powder and (ii) the composition and the preparation of the tape casting slurry. The preparation of a slurry is commonly carried out in two stages. First, the powder is deagglomerated and dispersed in the solvent with the aid of dispersants. Then binders and plasticizers are added and the slurry is homogenized. In order to obtain flat and dense components with a homogeneous microstructure, the ceramic particles have to be deagglomerated and well dispersed in the slurry.

In this study, two different Y-FSZ powders were used to give information on point (i), and one well-understood slurry system was used with various dispersants to investigate point (ii). The two powders are of high purity grades, although they have been produced in different ways and contain different types of impurities.

Tape casting slurries are very complex systems in which organic components interact.^{7,8} For instance, the adsorption of the binder onto the particle surface may prevent the dispersant from being adsorbed, thereby decreasing its effectiveness. An efficient dispersant in the powder/solvent

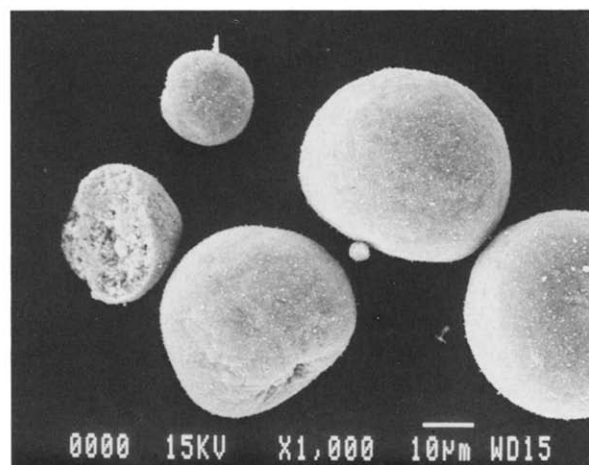
system does not necessarily act equally perfectly in the complete slurry system.

The aim of this study is also to identify efficient dispersants for zirconia particles in the complete tape casting slurry, and to verify that they do not impair the oxygen ion conductivity of the final membrane.

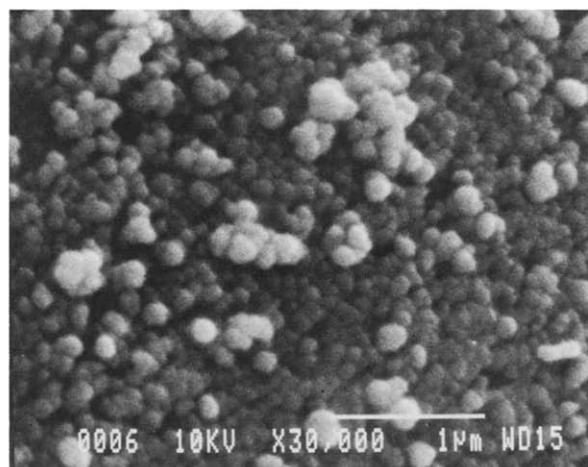
2 Experimental

2.1 Starting materials

Two fully yttria stabilized zirconia (8 mol% yttria) powders were used: TZ-8Y, Tosoh Corp., Japan (A) and 8Y-YSZ, a development product produced by coprecipitation from solution by Viking Chemicals, Denmark (B). These two powders contain different residues coming from the production process: powder A contains about 1000 ppm Na_2O , 400 ppm CaO and 1400 ppm Cl^- , whereas powder B contains 1.5 wt% polyvinyl alcohol but only 75 ppm Na_2O , 40 ppm CaO and very little Cl^- . The total metal impurity level except for Na and Ca is less than 500 ppm for both powders.



(a)



(b)

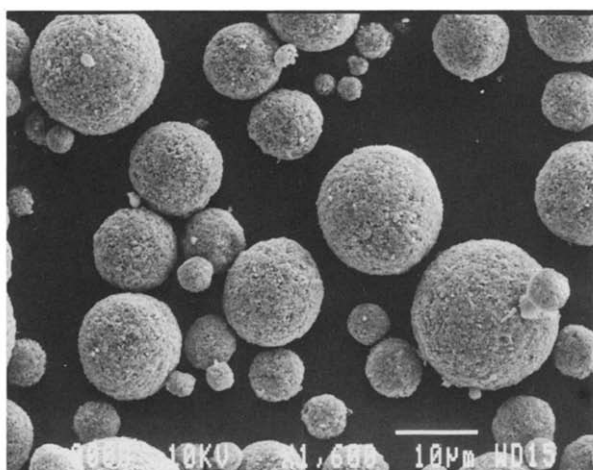
Fig. 1. Scanning electron micrograph of Y-FSZ (powder A) before deagglomeration, at (a) low and (b) high magnification.

These residues influence the surface properties of the powders.

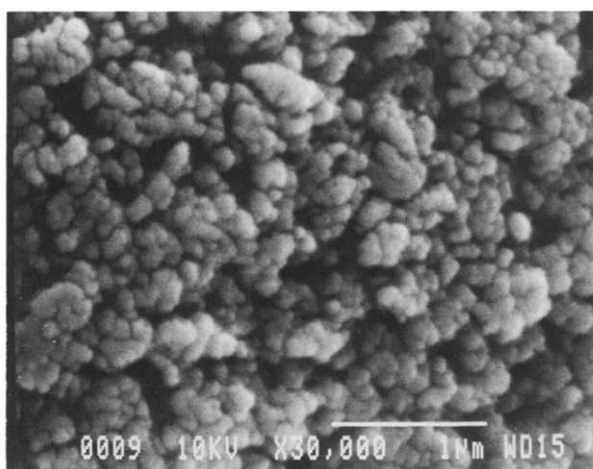
Both powders appear as spherical agglomerates with diameters ranging from 5 to 50 μm (Figs 1 and 2). At a smaller scale, both powders exhibit particles of about 0.2 μm in diameter with a rather homogeneous morphology. The surface area, measured according to the one-point BET method, was 15.7 and 29.0 m^2g^{-1} for powders A and B, respectively.

The solvent was an azeotropic mixture of 2-butanone and ethanol (MEK/EtOH). This medium polar solvent is compatible with many commonly used dispersants and has many advantages, e.g. the dissociation of phosphate ester is improved close to the azeotropic composition.⁹ Eleven common dispersants were used in this organic medium (Table 1).

For the study of the complete tape casting slurry, the binder was a polyvinyl butyral (PVB) (Butvar B98, Monsanto, St Louis, MO, USA) and the plasticizer was a mixture of polyethylene glycol (PEG) and phthalate (PHT).



(a)



(b)

Fig. 2. Scanning electron micrograph of Y-FSZ (powder B) before deagglomeration, at (a) low and (b) high magnification.

Table 1. Dispersant data and viscosity for Y-FSZ (powder A) dispersions in MEK/EtOH azeotrope, at 20°C and at a shear rate of 100 s^{-1}

Dispersant	Supplier	Viscosity (mPas)
Hypermer KD1	ICI, Kortenberg, Belgium	31
Beycostat C213 ¹⁰	CECA, Paris, France	37
Polyvinylpyrrolidone	Fluka Chemie, Buchs, Switzerland	50
Emphos PS 21 A	Witco Co., New York, USA	110
Hypermer KD2	ICI, Kortenberg, Belgium	2 100
Air treated capelin oil	Jahres Fabrikker, Sandefjord, Norway	2 500
Herring oil	Andelssild, Esbjerg, Denmark	2 800
Hypermer KD3	ICI, Kortenberg, Belgium	2 800
Capelin oil	Jahres Fabrikker, Sandefjord, Norway	3 000
Hypermer KD4	ICI, Kortenberg, Belgium	3 700
Menhaden oil	Spencer Kellogg, New York, USA	>10 000

2.2 Tape casting slurries

The compositions of the slurries are given in Table 2. The powder was first deagglomerated in the solvent with the dispersant, then the binder and plasticizer were added, and finally the homogenization was carried out by ball milling for 24 h. The slurry was kept rotating at a slow speed for deairing and to prevent settling.

2.3 Tape casting

Tape casting was performed with a laboratory tape casting bench (Cerlim Equipment, Limoges, France). Slurries were tape cast onto a fixed glass plate with a moving double blade device at a constant speed of 1 m min^{-1} . The blade height was 0.60 mm. After complete evaporation of the solvent, the powder concentration in the green tape was 81.6 wt% for powder A and 73.0 wt% for powder B.

2.4 Viscosity

The efficiency of dispersants was estimated from viscosity measurements in the system powder/solvent/dispersant. The dispersions were sonicated using an ultrasonic probe (VC600, Sonics & Materials, USA).¹¹ They were treated at 0°C for 3 min at an ultrasonic power of 600 W using a '50% pulsed mode', where pulses were emitted during 50% of the whole time. All viscosity measurements were carried out at the same time (4 h) after deagglomeration in order to obtain comparable results,

Table 2. Compositions of the tape casting slurries

Component	Slurry, powder A (wt%)	Slurry, powder B (wt%)
Y-FSZ powder (A/B)	55.40	45.25
MEK/EtOH	32.13	38.00
Dispersant	1.11	2.26
PVB	6.26	7.24
PEG	3.00	3.00
PHT	2.10	4.25

at 20°C and at various shear rates, using a rotating-cylinder viscometer (Haake Rotovisco RV 12, Germany).

2.5 Particle size analysis

The particle size distribution was analysed in the system powder/solvent/dispersant and in the complete tape casting slurry. The powders were deagglomerated and dispersed in the solvent with 2 wt% of dispersant, with the same procedure as for viscosity measurements. Before the measurements, the dispersions were diluted by pure solvent.

2.5.1 MEK/EtOH

Powders were sonicated in the azeotropic mixture with either a polymeric dispersant (Hypermer KD1) or a phosphate ester (Beycostat C213). The particle size distributions were determined by using either an X-ray granulometer (Sedigraph 5100, Micrometrics Inst. Co., GA, USA) or a combined sedimentation and optical transmission granulometer (Horiba Capa 700, Japan).

2.5.2 Tape casting slurries

Tape casting slurries were diluted by pure MEK/EtOH. The particle size distributions were determined by using the Horiba Capa 700 granulometer.

2.6 Density

The densities of the sintered plates were measured by Archimedes' method using cyclohexane as medium. Cyclohexane was used because its very low polarity reduces the risk of bubble formation at the surface of the plate. To avoid bubbles, which are often too small to be visible, is very important to obtain accurate results in the case of thin plates for which the surface/volume ratio is high.

2.7 Oxygen ion conductivity

The oxygen ion conductivity of plates was measured at 1000°C. A two-point AC method (longitudinal) was used as described elsewhere.¹²

3 Results

3.1 Dispersant screening

The viscosity of dispersions prepared with the various dispersants are given in Table 1. A large variation in viscosity was found. The composition of the dispersions was 69.0 wt% powder A, 29.6 wt% MEK/EtOH and 1.4 wt% dispersant (dispersant/powder = 2 wt%).

3.2 Dispersion of zirconia powders in MEK/EtOH

Of the eleven screened dispersants, three were shown to be very efficient in terms of viscosity:

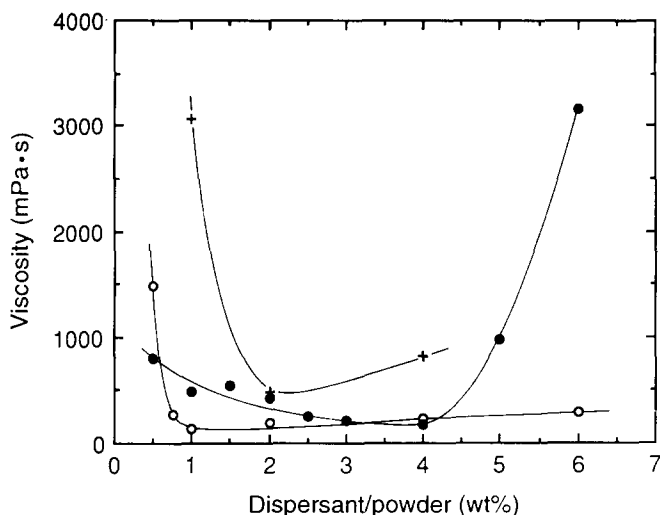


Fig. 3. Viscosity of dispersions of Y-FSZ (powder A) versus dispersant concentration at a shear rate of 100 s^{-1} for (○) KD1, (●) C213 and (+) PVP dispersants. The powder concentration was 80 wt%.

Hypermer KD1, Beycostat C213 and polyvinylpyrrolidone (PVP). To study their dispersing effect further, dispersions of powder A and B in MEK/EtOH azeotrope with varying dispersant concentrations were investigated.

Dispersions with powder A were prepared with a powder concentration of 80 wt% and dispersant/powder ratios varying from 0.5 to 6 wt%. To avoid too high viscosity, the powder concentration had to be lower for powder B. Dispersions with powder B were prepared with a powder concentration of 62.5 wt% and dispersant/powder ratios varying from 1 to 12 wt%. The evolutions of the viscosity of dispersions with powders A and B, versus dispersant concentration, are plotted in Figs 3 and 4, respectively. For each dispersant, the viscosity decreases with increasing concentration until it reaches a minimum. For powder B and

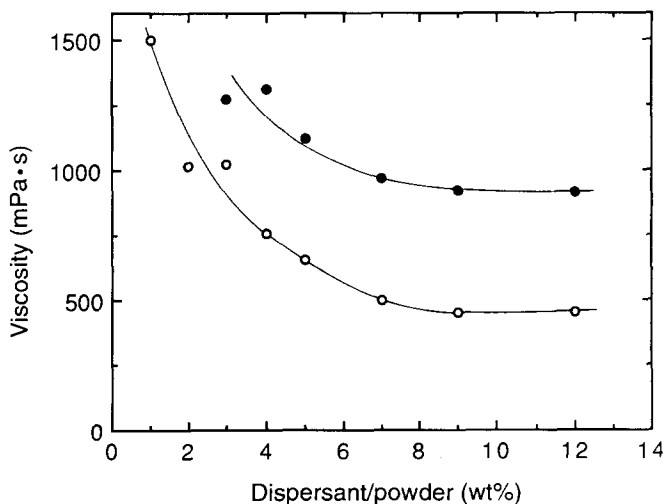


Fig. 4. Viscosity of dispersions of Y-FSZ (powder B) versus dispersant concentration at a shear rate of 100 s^{-1} for (○) KD1 and (●) C213 dispersants. The powder concentration was 62.5 wt%.

Table 3. Particle size data of Y-FSZ powders after ultrasonic treatment in MEK/EtOH with various dispersants^a

Powder	Dispersant	Mean particle size (μm)	Comments
A	Hypermer KD1	0.20	Narrow distribution
B	Hypermer KD1	6.00	Bimodal distribution, 2.5 and 10 μm
A	Beycostat C213	0.17	Narrow distribution
B	Beycostat C213	4.10	Bimodal distribution, 0.7 and 11 μm

^a The measurements were made using the Sedigraph 5100 after deagglomeration by ultrasound.

PVP as dispersant, the viscosity was too high to be measured with the reported method.

3.3 Particle size

Results from particle size measurements of powder A and B are shown in Table 3. Similar results were obtained for powder A in MEK/EtOH with KD1 and C213. Powder B was not completely deagglomerated before the measurements, resulting in bimodal particle size distributions and variable results. In Fig. 5, the evolution of the particle size of powder A in MEK/EtOH azeotrope is shown versus Hypermer KD1 concentration. The particle size decreases with increasing dispersant concentration until it reaches a minimum at 4–6 wt% dispersant.

3.4 Complete tape casting slurry

The complete tape casting slurry, including powder A, binder and plasticizer and using Hypermer KD1, PVP or Beycostat C213 as dispersants, was also considered. For all the slurries that were tested, the particle size remained almost constant at about 0.2 μm , even after several days of ageing.

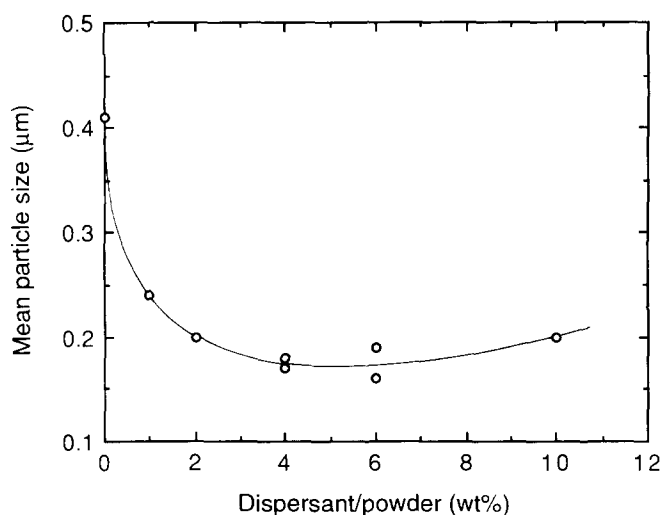


Fig. 5. Mean particle size of Y-FSZ (powder A) in MEK/EtOH azeotrope versus dispersant (Hypermer KD1) concentration. The measurements were made using Horiba Capa 700 after deagglomeration by ultrasound.

Table 4. Density of sintered plates^a

Starting powder	Dispersant	Density of sintered plate (g cm^{-3})
Grade A	Hypermer KD1	5.86 \pm 0.05
Grade A	Beycostat C213	5.86 \pm 0.05
Grade A	Polyvinylpyrrolidone	5.65 \pm 0.05
Grade B	Hypermer KD1	5.76 \pm 0.05
Grade B	Beycostat C213	5.72 \pm 0.05
Grade B	Polyvinylpyrrolidone	5.69 \pm 0.05

^a Theoretical density of zirconia with 8 mol% yttria is 5.97 g cm^{-3} .¹³

3.5 Tape casting and firing

Slurries were prepared with powder A and B using either Hypermer KD1, PVP or Beycostat C213 as dispersant. Since the tapes were bound to the glass plate during drying, the shrinkage at this stage occurred perpendicular to the surface. The shrinkage was about 70% in all cases. Square units (50 \times 50 mm^2) were cut from each green tape and heated in air at a rate of 0.5 $^{\circ}\text{C min}^{-1}$ to 500 $^{\circ}\text{C}$ and 5 $^{\circ}\text{C min}^{-1}$ from 500 to 1400 $^{\circ}\text{C}$. The samples were sintered at 1400 $^{\circ}\text{C}$ for 2 h. The shrinkage in the in-plane direction during sintering was 25 and 35% for plates made from powder A and B, respectively. Density values of sintered plates are given in Table 4. The density of plates made with KD1 and C213 was higher than that of plates made with PVP, indicating a better grain arrangement with KD1 and C213 as dispersants.

3.6 Oxygen ion conductivity

The oxygen ion conductivities of plates made from powder A are given in Table 5. The values show no significant difference between the three plates.

4 Discussion

4.1 Powder properties

The two powders studied in this work behave surprisingly differently in tape casting systems. Powder A disperses more easily, makes tape casting slurries with higher ceramics loading and produces sintered bodies with higher density than

Table 5. Oxygen ion conductivity, at 1000 $^{\circ}\text{C}$, of plates made from powder A with three dispersants used for deagglomeration and dispersion of the ceramic particles in the tape casting slurry

Dispersant	Oxygen ion conductivity at 1000 $^{\circ}\text{C}$ (S cm^{-1})
Hypermer KD1	0.17 \pm 0.02
Beycostat C213	0.16 \pm 0.02
Polyvinylpyrrolidone	0.19 \pm 0.02

powder B. Powder A can make low-viscosity dispersions with a high solids loading and with a dispersant concentration as low as 0.5% (dispersant to solid ratio), whereas too high dispersant concentrations in the range 4 to 8% are necessary in the case of powder B. Granulometric characteristics of the two powders are similar and the BET surface areas differ only by a factor less than two. Important factors other than particle size and surface area contribute to the behaviour of powders in tape casting systems. In particular, the presence of different surface impurities in the two powders contribute severely to the difference in their dispersing properties, e.g. Na^+ , Ca^{2+} and Cl^- in powder A and PVA in powder B.

4.2 Dispersants

The eleven different dispersants that were screened in this study showed great variations with respect to efficiency. Hypermer KD1, polyvinylpyrrolidone (PVP) and Beycostat C213 were shown to be superior to the remaining eight for viscosity reduction. A dispersant's ability to reduce the viscosity is a good indicator for its dispersing effect.¹⁴ PVP is slightly less efficient than KD1 and C213. KD1 and PVP are polymeric dispersants whereas C213 is a phosphate ester. It is somewhat surprising that the fish oils, and especially the menhaden oil, do not seem to be efficient. These unsaturated fatty acids are often referred to in the literature and are used in industry as dispersants for tape casting, especially for barium titanate and alumina. They do not seem to work well with zirconia in medium polar solvents like ketone/ethanol azeotrope.

With powder A, the minimum viscosity was obtained at 1% (dispersant to solid ratio) for KD1. This point of minimum viscosity (PMV) was about 2% for PVP and 3–4% for C213. For C213, a sharp increase in viscosity was observed at concentrations above this limit, indicating bridging flocculation. This was not observed for KD1.

In contrast to the PMV of 1% for KD1 it was found by particle size measurements that the minimum particle size was obtained with 4–5% KD1. This is somewhat surprising as it is often found in ceramic dispersions that the PMV and the point of minimum particle size overlap. In this case however, increasing the dispersant concentration from 1 to 4% leaves the viscosity almost constant while the particle size is reduced by 25%.

This observation may be attributed to remaining porous agglomerates at 1% KD1, trapping solvents which do not contribute to the dispersion. At 4% KD1, these agglomerates are broken down, and the solvent is liberated. Another effect which may contribute is the fact that the viscosity

measurements were carried out with much more concentrated samples (80 wt% powder) than in the case of the particle size measurements (about 1 wt% powder).

4.3 Tape casting

The addition of binder and plasticizers to the dispersions did not cause reagglomeration. This was found by particle size measurements of aged slurries. All tape casting slurries prepared with the three successful dispersants were very stable, with no sign of reagglomeration even after several days on the shelf.

Green tapes prepared from powder A were sintered up to 98% of the theoretical density at 1400°C when KD1 and C213 were used as dispersant. With PVP, a lower density was obtained (95%). The same was found for powder B, although this powder sinters to a lower maximum density (95–96%). These results indicate that the particle packing is not as efficient with PVP as with the other two dispersants. The results shown in Fig. 3 agree with this observation: the minimum viscosity is lower for KD1 and C213 than for PVP, indicating a better dispersing effect, leading to a closer particle packing in the green tape, and finally resulting in a higher sintered density with KD1 and C213 than with PVP.

4.4 Oxygen ion conductivity

The oxygen ion conductivity was measured for sintered plates prepared with the three different dispersants (KD1, C213 and PVP). No significant difference was found between the three dispersants. The values obtained, 0.16–0.19 S cm^{-1} at 1000°C, are in agreement with values reported in the literature: 0.158 S cm^{-1} ,¹² and 0.15 S cm^{-1} .¹⁵ Thus, the use of a phosphate ester in the green tape, possibly leaving traces of phosphorus in the sintered plate, do not impair the oxygen ion conductivity.

5 Conclusions

Dispersion studies with two different powders of fully yttria stabilized zirconium oxide in ethanol/ketone azeotrope have revealed that there are important factors other than surface area and particle size that contribute to the behaviour of powders in tape casting systems. One such important factor is the presence of impurities at the surface of the particles. Of eleven screened dispersants, only three were shown to be efficient: two polymeric dispersants (ICI Hypermer KD1 and polyvinylpyrrolidone, PVP) and a phosphate ester (Beycostat C213). PVP shows slightly less dispers-

ing effect than KD1 and C213. The addition of binder and plasticizers to the dispersions to form tape casting slurries did not cause reagglomeration. Sintered plates cast from slurries prepared with KD1, PVP or C213 as dispersant had high and about equal oxygen ion conductivity ($0.16\text{--}0.19\text{ S cm}^{-1}$ at 1000°C). Thus, the use of a phosphate ester in the green tape, possibly leaving traces of phosphorus in the sintered plate, did not impair the oxygen ion conductivity. Fish oils, and especially menhaden oil, were not efficient dispersants with zirconia in the solvent system that was studied.

Acknowledgement

This work was carried out as a part of NORD-TAPE—Nordic Project for Tape Casting of Ceramics—with financial support from Nordic Industrial Fund and the Royal Norwegian Council for Industrial and Scientific Research (NTNF).

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