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Powder dispersion and aqueous tape casting of YSZ-NiO composite

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Powders of YSZ and NiO were prepared by precipitation of hydroxides, calcination and wet grinding. The dispersion conditions were optimized from zeta-potential and viscosity studies. Aqueous suspensions of both the powders exhibited maximum zeta-potential values in two ranges of pH, 3 to 4 (positive) and 9 to 11 (negative), establishing the feasibility of a dispersion of both oxides together. Viscosity measurements indicated presence of effective dispersion of a 1:1.5 mixture of YSZ:NiO below a solid concentration of 25 volume percent. Aqueous tape cast slurries were formulated using PVA solution as binder and glycerol as plasticizer. The rheological behavior of these slurries (viscosity and visco-elastic parameters) was strongly influenced by slight variation in the solid content. Visco-elastic measurements revealed all the slurries to be predominantly viscous and become more elastic with increasing solid content. Defect free flat tapes could be obtained by casting the slurry with optimum flow characteristics (i.e., pseudoplastic but non-thixotropic) that could be sintered to flat sheets with 80% T.D. (theoretical density) and 20% O.P. (open porosity) at 1450°C. Upon reduction in hydrogen at 1000°C, it formed in to YSZ-Ni composite that retained the same micro structural features of YSZ-NiO.

1. Introduction

Porous tapes (50 to 500 micron thick) of yttria stabilized zirconia-nickel (YSZ-Ni) composites find application as anode materials in the planner type solid oxide fuel cell (in both electrolyte and electrode supported designs) [1]. The various physico-chemical properties making this system as the anode material has been reviewed by Minch [2]. It is due to its desirable properties such as stability and high electronic conductivity in hydrogen atmosphere, thermal expansion coefficient similar to YSZ electrolyte and ability to catalyze the reaction of hydrogen and oxide at the triple phase junction—YSZ, Ni and gaseous H_2 [3]. The Ni serves both as an electro catalyst and electronic conductor while the YSZ provides stability to the structure and keeps the nickel particles dispersed. The advantages of anode-supported designs are many. Concentration polarization is lower since the effective binary diffusivity of H_2 (anode) gas is typically three times greater than that of air. The presence of metallic nickel leads to a better thermal shock resistance due to its higher thermal conductivity and plasticity.

The YSZ-Ni anode is generally formed by the reduction of the nickel oxide in YSZ-NiO to nickel as it readily creates the requisite porosity and desired microstructure. An additional advantage is the ease of processing of oxide slurries into tapes. Hence formation of YSZ-NiO thin sheets by tape casting is an aspect worthy of study. Even in porous bodies, homogeneity of microstructure is key to their successful performance in the application and life. The powder characteristics and processing conditions (especially dispersion conditions) need to be optimized to form flat tapes with the desired amount of porosity in the processing temperature range (1400 to 1500°C) for both anode and electrolyte supported designs.

Well-dispersed slurries yield tapes with homogeneous microstructure. The state of dispersion in oxide slurries is characterized by the zeta-potential and viscosity of the suspensions. As these parameters are surface chemistry dependent, they are strongly influenced by the preparation conditions for any given oxide powder. Synthesis of porous tapes of ZrO_2-Y_2O_3 and [(ZrO_2-Y_2O_3)-(CeO_2-Gd_2O_3)-NiO] systems using non aqueous media (dispersant, binder, plasticizer and solvent) have been reported [4, 5]. Advantages of aqueous tape casting are many—less toxic and environmental friendly process. However, a detailed study on the evaluation of dispersion conditions (through a detailed study of zeta potential and rheological parameters) for formulation of aqueous slurry for tape casting of YSZ-NiO composite (thickness in the range of ∼100 to 400 μm) and the characteristics of the sintered tapes has not yet been reported and hence studied.

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2. Experimental

The hydroxide gel corresponding to zirconia—8m% yttria composition was co-precipitated by the reverse strike technique using ammonia bath (0.1 M) and solution of zirconium oxy-chloride (0.1 M) containing desirable amount of yttrium nitrate. The precipitate was filtered, washed repeatedly (four times) with distilled water to remove chloride ions and finally dried in an air oven at 70°C. The granules of agglomerated dried gel were broken into a powder mass of size <100 μm and was planetarily dry ground for 1 h. The nickel hydrous oxide was precipitated from nickel nitrate (0.1 M) solution using stoichiometric amount of ammonia and refluxing at 85°C for 3 h. The precipitate was filtered, repeatedly washed (four times) and oven dried. The dried precipitate as such was found to be a fine powder.

Both the powders were calcined at 900°C to form into chemically pure YSZ and NiO. The YSZ powder was ground to the size of the as calcined NiO powder. Both these powders were further calcined at 1350°C for 2 h and wet ground for 1 h to form into same size. The particle size distribution of the powders was evaluated by the laser light scattering technique. The aqueous suspensions of 1350°C calcined YSZ and NiO powders were evaluated for their zeta potential variation as a function of pH (using nitric acid and ammonia) by laser Doppler velocimetry. The powder mixture of YSZ-NiO (weight ratio of 1:1.5) was dispersed in water (pH $\sim$ 3 to 4) by ball milling for 4 h followed by addition of binder (poly vinyl alcohol) and plasticizer (glycerol). This mixture was further mixed for 20 h by ball milling for formulation of tape cast slurries. The compositions of the tape cast slurries characterized are given in Table I. The viscosity variation with shear rate for the slurries without and with binder addition was studied using a cone and plate viscometer. Dynamic measurements (variation of elastic and viscous modulei with amplitude of shear stress from 3 to 50 Pa at a fixed frequency of 0.17 Hz) were carried out to characterize the internal structure of the slurries. The viscosity data for the tape cast slurries was fitted using the Casson model—[$\sigma^{1/2} = \sigma_0^{1/2} + (k\gamma)^{1/2}$ where σ is the shear stress, γ is the shear rate, σ_0 is the Casson yield stress, k, a constant, is the Casson viscosity]—to obtain the yield stress (Table II).

TABLE I In all slurries the weight ratio of powder (YSZ-NiO):binder (PVA):plasticizer (glycerol) was 85:10:5

Name of slurry	Volume percent of powder with respect to total water content
A	18
B	16
C	14

TABLE II Yield stress, k (Casson viscosity) and correlation coefficient for the tape cast slurries

Name of the slurry	σ_0 (Pa)	k	Corr. coefft.
A	3.77	1.58	0.998
B	1.79	1.1	1
C	0.34	0.72	1

Tape casting was done in a laboratory-assembled set up at a casting rate of 5 to 10 mm per second with varying slurry thickness (100 to 500 micron gap). The tapes were dried overnight and cut into required size (up to 7.5 cm diameter). The binder was burnt out at a slow rate of heating (0.5°C/min) up to 600°C in air followed by sintering up to 1450°C (at a rate of heating of 5°C/min). Sintering was done by keeping the tapes in between thin YSZ insulation fiber boards. The sintered tapes were reduced in hydrogen at 1000°C to form into nickel. They were characterized for their green density by dimensional measurement, sintered density and open porosity by Archimedes method, phase formation by XRD and microstructure by SEM.

3. Results and discussion

Reverse strike co-precipitation of YSZ was followed as it is expected to improve the compositional homogeneity (both zirconium and yttrium) in the jelly precipitate. The oven dried precipitate was an agglomerated mass and dry ground to form into powder. The nickel hydroxide precipitate was found to be a granular one and formed into an easily friable powder upon oven drying. Thus agglomeration took place during drying in the jelly YSZ hydroxide precipitate but not in the case of granular hydrated nickel oxide. Both the precursors of YSZ and NiO were calcined at 900°C to form into chemically pure oxides. The particle size distributions of the differently treated powders are shown in Fig. 1. The 900°C calcined NiO powder as formed possessed a mean size (D_{50}) of $\sim$2.5 μm. The YSZ powder exhibited a mean size of 6 μm with substantial amount (30%) of coarse agglomerates in the range of 10 to 100 μm, which can introduce micro structural heterogeneities and defects in the tapes. Hence it was wet ground to a mean size of 2.5 μm with all particles below 10 μm. Calcination at this intermediate temperature made grinding to the desired size ($\sim$2.5 μm) easier. During wet grinding of YSZ, un-calcined powders reacted with water due to hydration while that calcined

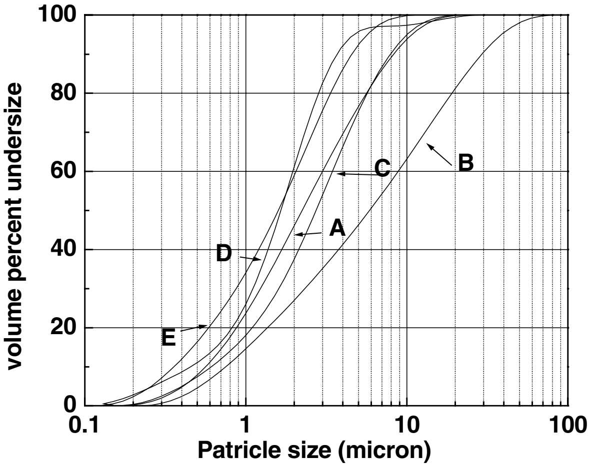

Figure 1 Particle size distribution of powders: A—Nickel oxide hydrate calcined at 900°C, B—YSZ gel dry ground and calcined at 900°C, C—'B' wet ground for 1 h, and D, E—'A' and 'C' calcined at 1350°C and wet ground for 1.

at 1350°C was very difficult to be ground. Thus calcination at 900°C enabled easy grinding of coarse agglomerates (size > 10 μm). Final calcination at 1350°C increased solid content in slurries and reduced the extent of shrinkage during drying and sintering of tapes, desirable for formation of defect free bodies. The particle size distribution of the 1350°C calcined powders of YSZ and NiO after grinding for an hour remained essentially the same ($\sim$2.2 μm) indicating absence of further formation of strong inter-agglomerate bonding at 1350°C. Thus calcination at 1350°C resulted in sintering of the individual particles improving their density and hence the solid loading in slurries.

The zeta potential variations with pH for the 1350°C calcined YSZ and NiO suspensions are shown in Fig. 2. Suspensions of YSZ powder were better charged in the pH range of 9 to 11 ($\sim$30 mV) than in the pH range of 3 to 4 ($\sim$20 mV). The higher this value the better is the colloidal stability through electrostatic repulsion. Suspensions of NiO were better charged in the pH ranges of 3 to 4 ($\sim$40 mV) than in the pH range of 9 to 11 (30 mV). One salient observation of this result is that a dispersion of both the oxides together is stable in both the ranges of pH (3 to 4 and 9 to 11) due to their like-charged nature. This is a prerequisite for the formation of stable dispersion in formulation of tape cast slurries of composites. It has been reported that trace amount of chloride ions present in the YSZ powder obtained by co-precipitation can drastically alter the dispersion behavior [6]. There is a wide variation in the reported zeta potential values of YSZ suspensions [6, 7]. Calcination temperature influences the reactivity of the surface with water and the distilling away of the impure ions. The variation in the reported values of zeta potential for YSZ could be attributed to the above facts. There is no report on the zeta potential of NiO suspensions for comparison and we have found that an acidic dispersion is more stable than an alkaline one. Honoviet *et al.* have presented a detailed description of the origin of zeta potential in oxide suspensions [8]. It depends upon the pH of the slurry, the concentrations of the adsorbed ions and their nature. The reaction of surface of oxide particles in aqueous slurries result in formation of amphoteric hydroxide group, MOH, which can react with H^+ and OH^-. A value greater than 20 mV is an indication of the deflocculated state and higher the value better is the dispersion stability. In our studies, the exact values of zeta potential of the suspensions of both the powders were found to be influenced by the calcination temperature (decreased with increasing calcination temperature) which could be attributed to the variation in surface composition and its reactivity with the dispersing medium—water. However, the pH ranges of dispersion stability (3 to 4 and 9 to 11) remained the same.

The plots of variation of viscosity with shear rate for slips containing varying volume percent (25 and 35) of solid concentration of powder mixtures of YSZ and NiO in water at varying pHs (3 and 10) is shown in Fig. 3. The viscosity decreased with decreasing solid content and the flow behavior becomes less shear thinning (i.e., Newtonian from pseudoplastic). Even at the point of maximum zeta-potential, flocculates are reported to be present in concentrated slurries and this is

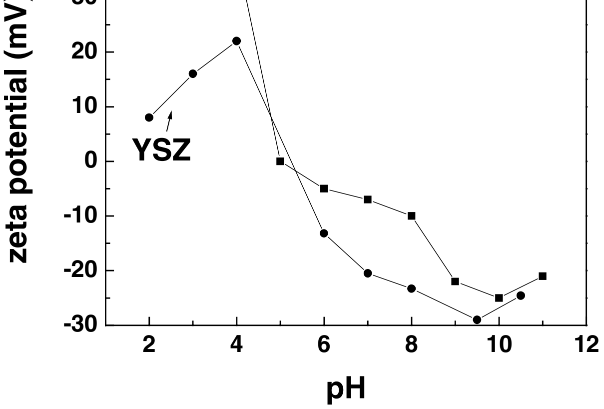

Figure 2 Zeta-potential variation with pH of aqueous suspensions of YSZ and NiO calcined at 1350°C.

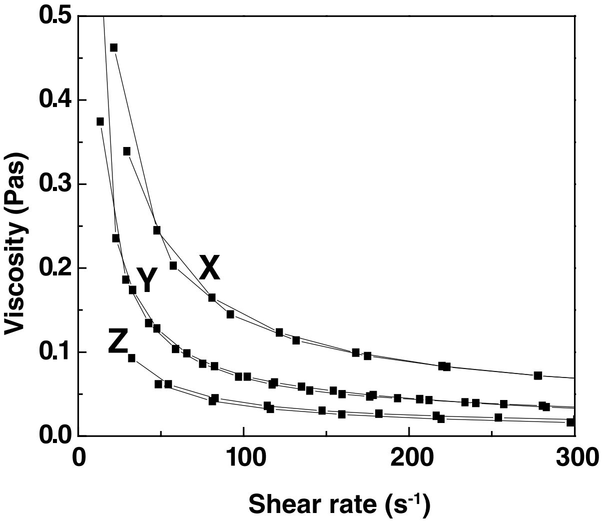

Figure 3 Variation of viscosity with shear rate for YSZ-NiO slurries with varying solid content and pH (X-35 vol% solid & pH $\sim$ 3; Y—25 vol% solid and pH $\sim$ 10; Z—25 vol% solid and pH $\sim$ 3).

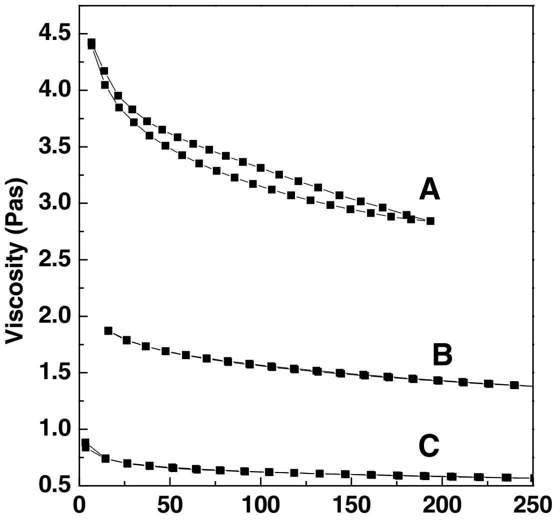

Figure 4 Variation of viscosity with shear rate for YSZ-NiO tape cast slurries with varying solid concentration (A, B, C).

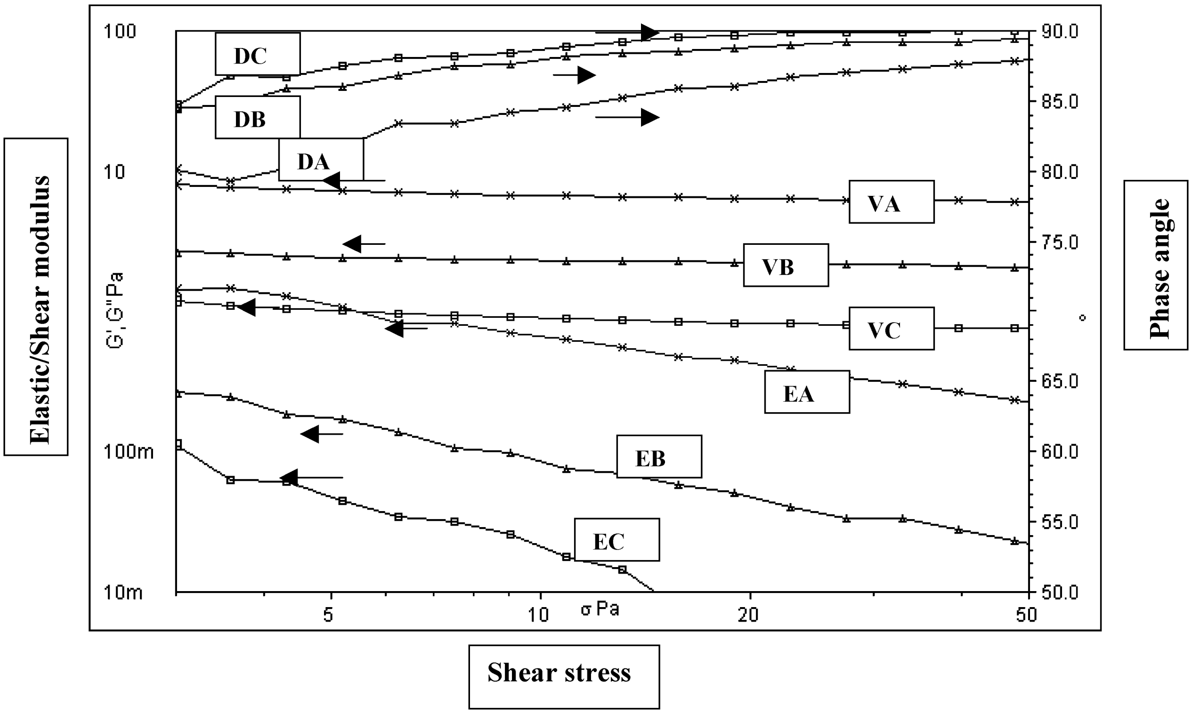

Figure 5 Variation of elastic modulus, viscous modulus and phase angle with increasing amplitude of shear stress for the tape cast slurries A, B, C at 0.17 Hz (E, V, D represent elastic modulus, viscous modulus, phase angle respectively).

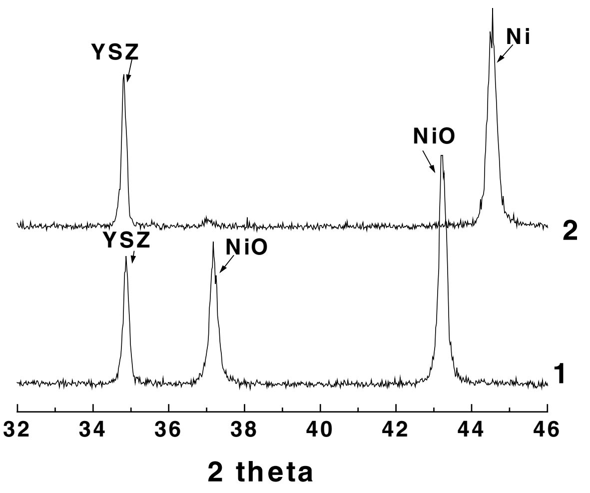

Figure 6 XRD patterns for YSZ-NiO tapes—[(1)-sintered and (2)-reduced].

exhibited by their rheological behavior [8]. The pseudoplastic flow behavior (shear thinning) is attributed to the presence of flocculates that break upon shearing. The flocculates trap liquid inside their structure making it not available for dilution i.e., resulting in higher viscosity. Upon shearing the flocculates break making the liquid available for reducing viscosity. Even though dispersion is expected to be favored at both alkaline and acidic pHs as per zeta potential values, viscosity of slurries with pH 3 is lesser than that of slurry with pH 10 (Fig. 3), indicating better degree of dispersion in acidic medium. Shear rate independent flow behavior is an indication of effective dispersion of individual particles in the slurry. The effective powder dispersion before the addition of binder is an important aspect as afterwards only mixing could occur due to increased viscosity. This aspect has been emphasized in the study of tape casting of alumina by Gutierrez *et al.* [9]. Thus the slurry with 25 vol% YSZ-NiO at a pH of 3 ground for 4 h was used for formulating the tape cast slurry.

The minimum amount of binder (PVA) and plasticizer (glycerol) required to form flexible tapes was found to be about 10 and 5 wt% with respect to solid content. Hence a detailed study of the rheological behavior of the tape cast slurries with this composition was carried out. The variation of viscosity with shear rate for the slurries of above composition (powder–binder–plasticizer) with varying amount of water is shown in Fig. 4. The slurry containing 25 vol% solid in water exhibited shear rate independent flow behavior, characteristic of ideal dispersion (Fig. 3). Addition of binder solution to the powder slip increased the viscosity by an order of magnitude and introduced shear rate dependency (pseudoplasticity) even though the solid concentration reduced. This is generally attributed to the particle–binder–water interactions [10]. Another salient observation is with each 2 vol% increase in solid content, the viscosity increased drastically and resulted in larger variation in the values during increase and decrease of shear rates (i.e., introduced thixotropy). Slurry-A was found difficult to be mixed and de-aired, and exhibited thixotropy. Generally, uncontrolled flow of slurry occurs with slip of lower solid content while removal of entrapped air bubble and flow under very high shear rates make undesirable the slurries with higher solid concentration from tape casting point of view [10]. The analysis of the viscosity data by Casson Model exhibited that the yield stress increased with increasing solid content of the slurry indicating the increase in the degree of flocculation of the slurry (Table II). Still the values are less than that resulting in the casting rates used for tape casting. The values of

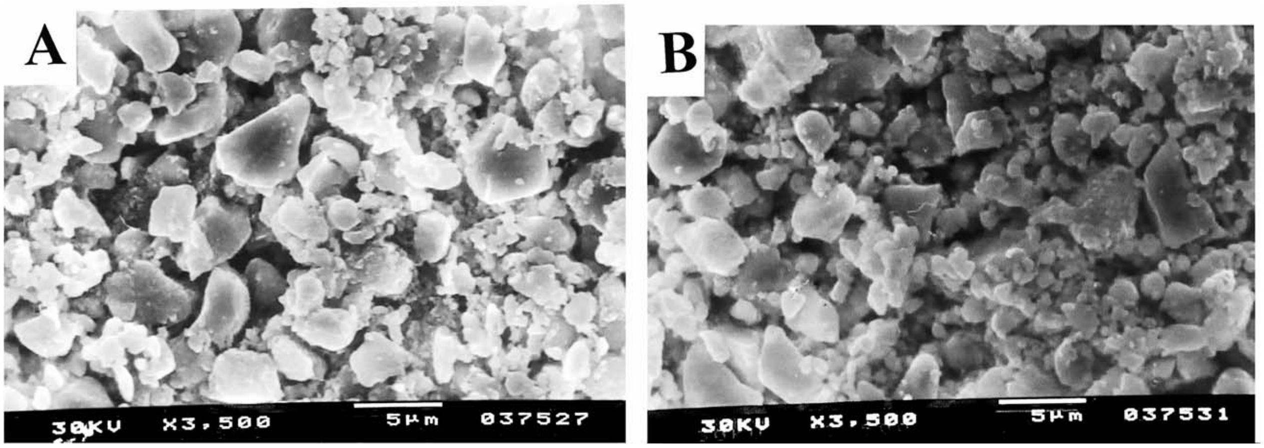

Figure 7 SEM surface morphologies of porous tapes: A—YSZ-NiO tape sintered at 1450°C and B—YSZ-Ni tape formed by reducing 'A' in H_2 at 1000°C.

correlation coefficients obtained were near unity, indicating the validity of this model to describe the flow behavior of these slurries.

The variations in the visco-elastic parameters (elastic and viscous modulei and phase angle) with increase in stress of the slurries (A, B, C) are shown in Fig. 5. For all the slurries, the elastic modulus was lesser than the viscous modulus indicating all of them are predominantly viscous materials. Such a predominant viscous behavior has been observed with slurries of alumina formulated using water soluble binders such as PVA [11]. The elastic modulus decreased and the phase angle increased to 90° while the viscous modulus remained nearly constant with increasing stress. This could be attributed to the breaking away of the internal structure of the slurries with increasing stress. The increase in the individual modulei values, the ratio of elastic to viscous modulei and increase in the deviation of the phase angle from 90° with increasing solid content of the slurry are attributed to their increased elasticity. The slurry-B exhibited desirable amount of pseudo-plasticity required for tape casting. The viscosity was high enough to avoid sedimentation of particles during drying of the wet tapes and still low enough for easy removal of air bubbles. The tapes formed using this slurry were flat after drying and sintering.

The green density of the tapes obtained from dimensional measurements was about 60% T.D. indicating the compact packing of the dense particles in the tape. Slow rate of heating (0.5°C/min) was essential for burning out the binder from the dried tapes without introduction of defect. Sintering at 1450°C for 3 h resulted in tapes with desired density (80% T.D.) and open porosity (20%) (as determined by Archimedes method; the theoretical density of the composite was assumed as the weighed average of the theoretical densities of YSZ and NiO–6.4 g/cc), which is a requirement for their use in the forming of the anode or electrolyte supported designs of fuel cells. The sintered tape was found to be a mixture of YSZ and NiO while that reduced in hydrogen is a mixture of YSZ and Ni (Fig. 6). The typical microstructure of the sintered tapes exhibited the composite structure with connected pores (Fig. 7A and B). The nickel clusters formed by reduction retained the same microstructure of YSZ-NiO tapes.

4. Conclusions

YSZ and NiO powders with desired characteristics were prepared by precipitation methods followed by calcination and grinding. The dispersion conditions were optimized through zeta-potential and viscosity measurements. Both the powders exhibited maximum charge in acidic (pH ∼ 3 to 4) and alkaline (pH ∼ 9 to 11) media, establishing the stability of a dispersion of both together at these pH ranges. The slurry composition for formation of quality tape was optimized through rheological measurements (viscosity and visco-elastic measurements). Slurry—B exhibited pseudoplasticity without thixotropy and was predominantly a viscous material. The tapes could be sintered flat and reduced to form YSZ-Ni bodies with the desired microstructure. This study outlines the processing conditions to form porous flat tapes of YSZ-Ni composite using aqueous tape casting.

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References

1. SOREN LINDEROTH, NIKOLAOS BONANOS, KARIN V. JENSON and JORGEN B. BLIDE SORENSON, *J. Amer. Ceram. Soc.* **84** (11) (2001) 2652.
2. NGUYEN Q. MINH, *ibid.* **76**(3) (1993) 563.
3. SUN-JAE KIM, WONHEE LEE, WON-JUN LEE, SOON DONG PARK, JAE SUNG SONG and EUN GU LEE, *J. Mater. Res.* **16**(12) (2001) 3621.
4. JULIA WILL, MARTIN K. M. HRUSCHKA, LORENZ GUBLER and LUDWIG J. GAUCKLER, *J. Amer. Ceram. Soc.* **84**(2) (2001) 328.
5. STEPHEN F. CORBIN, JOYCE LEE and XINQIAO, *ibid.* **84**(1) (2001) 41.
6. RAJENDRA N. BASU, CLIVE A. RANDALL and MARRILEA J. MAYO, *J. Amer. Ceram. Soc.* **84**(1) (2001) 33.
7. M. M. SEABAUGH, S. L. SWARTZ and W. J. DAWSON A Report on 'Tubular SOFC with Deposited Nanoscale YSZ Electrolyte,' www.nextechmaterials.com

8. DAVID HOUIVET, JAAFAR EL FALLAH and JEAN-MARIE HAUSSONNE, *J. Amer. Ceram. Soc.* **85**(2) (2002) 321.
9. CARLOS A. GUTIERREZ and RODRIGO MORENO, *Mater. Res. Bull.* **36**(2001) 2059.
10. BERND BITTERLICH, CHRISTIANE LUTZ and ANDREAS ROOSEN, *Ceram. Intern.* **28**(2002) 675.
11. A. KRISTOFFERSSON, E. RONCARI and C. GALASSI *J. Europen. Ceram. Soc.* **18**(1998) 2123.

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