

Aqueous tape casting of SDC with a multifunctional dispersant

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To reduce the surface tension of water, aqueous tape casting of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC) was performed using triethanolamine (TEA) as a dispersant that also acted as a surfactant, with polydimethyl siloxane as a defoamer. TEA and polyvinyl alcohol (PVA) binder were pre-dissolved and added in a dilute stage to guarantee a homogeneous distribution of the slurry. Zeta potential studies showed that the isoelectric point (IEP) of SDC particles moved from $\text{pH} = 3.69$ to $\text{pH} = 4.29$ after 2 wt.% TEA (based on the SDC powder) was added, while absolute value of the zeta potential reached a maximum value at $\text{pH} \approx 10$. The slurry with 60 wt.% solid content exhibited a typical shear thinning behavior. Flexible and homogeneous green tapes with smooth surfaces were obtained after drying. The SDC green tapes with a high green density of 56.9% exhibited an ultimate tensile strength of 1.39 MPa and a strain to failure of 52%.

Key words: Aqueous tape casting, SDC, TEA, Dispersant, Surface tension.

Introduction

Two approaches have been proposed to reduce the operating temperature of solid oxide fuel cells (SOFCs): the first is the use of alternative electrolyte materials with higher ionic conductivity instead of yttria stabilized zirconia (YSZ) at a reduced temperature, such as doped ceria; the second is a reduction in the thickness of the electrolyte [1-3]. It would be better if both of the approaches are simultaneously taken.

To realize the first approach, doped ceria has been considered, for it is one of the most promising electrolyte materials for intermediate temperature SOFCs due to its higher ionic conductivity than YSZ at a relatively low temperature. Among the various doped ceria such as with La_2O_3 , Nd_2O_3 , Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , Tm_2O_3 , Yb_2O_3 and Y_2O_3 doped ceria, Sm_2O_3 doped ceria (SDC) was found to have the highest ionic conductivity [3-5]. To realize the second approach, many film preparation techniques such as tape casting, screen printing, spray pyrolysis and plasma spray have been used. Tape casting is a cost-effective forming technique for producing thin, flat and large area ceramic tapes of usually 10-1000 μm thickness [6-7]. The most common way to perform tape casting is to use slurries based on organic solvents. However, the volatility and toxicity of these solvents lead to many studies of an aqueous tape casting process. In recent years, many aqueous tape casting processes have been reported [6-8]. Compared with organic solvent based slurries, aqueous ones have some drawbacks such as slow drying of the tapes,

higher crack sensitivity, flocculation and poor wetting of the slips due to the high surface tension of water [9-10]. To reduce the high surface tension of water, some papers have reported using special surfactants for aqueous tape casting [6-7].

In this study, triethanolamine (TEA) was used as a dispersant, which also played a role of an excellent surfactant that can reduce the surface tension of water. So a special surfactant was avoided. A homogeneous mixture of the powder, the solvent and the additive components is a prerequisite for the manufacture of a defect-free green tape. This requires a careful selection and an accurate control of the processing to prepare well-dispersed and stabilized slurries. The influence of the pH, the dispersant, the binder, the plasticizer and the solid content on the stability of SDC slurries through zeta potentials and rheology was studied. Glycerol was selected as the plasticizer for PVA. The tensile properties and green density of the green tapes were also studied to evaluate the mechanical properties and compactness of the green tapes.

Experimental

Materials

$\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ was synthesized by a spray pyrolysis technique [11]. The particle size was in the range 0.5-3 μm . Distilled water was used as a solvent. The dispersant used for slurry stabilization was triethanolamine (TEA, A.R., Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) with a molecular weight of 149.19 $\text{g} \cdot \text{mol}^{-1}$. Glycerol (A.R., Tianjin Kernel Chemical Reagent Co., Ltd, Tianjin, China) with a molecular weight of 92.09 $\text{g} \cdot \text{mol}^{-1}$ was used as a plasticizer. The binder chosen was polyvinyl alcohol (PVA, A.R., Sinopharm Chemical Reagent Co.,

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Ltd, Shanghai, China) with a molecular weight of $170000\text{--}180000\text{ g}\cdot\text{mol}^{-1}$. Polydimethyl siloxane fluid (A.R., Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China) was used as a defoamer. The pH value of the suspensions was adjusted by HCl (A.R., Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) and $\text{NH}_3\cdot\text{H}_2\text{O}$ (A.R., Kaifeng Dongda Chemical Co., Ltd). KCl (A.R., Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) was used to adjust the ionic strength of the suspensions for zeta potential tests.

Zeta potential tests

In order to understand the relationship between the dispersant content, the pH value of suspensions and the zeta potential, zeta potential values of the SDC suspensions were tested with a zeta potential analyzer (Brookhaven Instruments Co., USA). The suspensions were prepared by dispersing the SDC powder (0.02 wt.%) in distilled water both in the absence and presence of the dispersant at various pH levels. The ionic strength of each suspension was adjusted by using an 0.001 M KCl solution. The pH levels were then adjusted with analytically pure grade HCl (0.1 M) and $\text{NH}_3\cdot\text{H}_2\text{O}$ (1 M). The pH value was measured by a pH meter (PHS-3CT, Shanghai Jinmai Equipments & Meters Co., Ltd, Shanghai, China). Before the tests, the suspensions were ultrasonically mixed for 30 minutes to ensure the deflocculation and equilibrium between the particle surfaces and the dispersant.

Rheological measurements

The rheological behaviors of the slurries with various solid (the SDC powder), binder, plasticizer contents and optimum dispersant content at a constant pH value were characterized using a rotary viscometer (Brookfield DV-II, Brookfield Engineering Laboratories, Inc., USA). Before starting a measurement, a pre-shearing was applied at a high shear rate (400 s^{-1}), followed by a 2 minute rest in order to avoid an undesired influence from different mechanical histories. The shear dependence behavior of the slurry examined under steady shear conditions was evaluated by ascending and descending shear rate ramps from 0 s^{-1} to 300 s^{-1} in 3 minutes and from 300 s^{-1} to 0 s^{-1} in 3 minutes, respectively.

Tape casting

A flowchart of the tape casting process is shown in Fig. 1. Initially, distilled water (30 wt.% surplus) was mixed with the optimum content of TEA by mechanical stirring for 2 minute. Then the SDC powder was added and mechanically stirred for 30 minutes with the pH value adjusted to about 10. Subsequently, the slurry was ball milled for 20 h. In order to achieve a more uniform dispersion of the binder, PVA was pre-dissolved in an appropriate amount of distilled water. To assure complete dissolution of all the PVA, the solution was heated to $95\text{ }^{\circ}\text{C}$ for at least 2 h and stirred in a hot

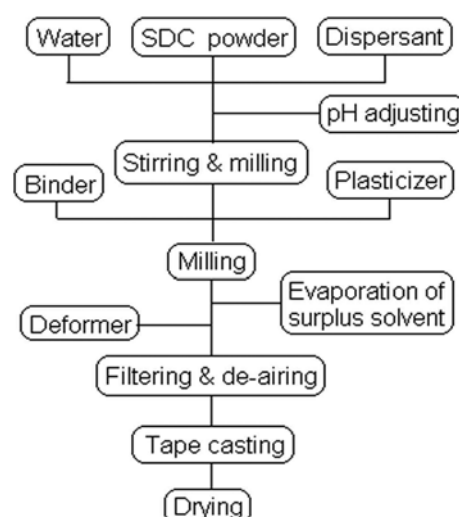


Fig. 1 Flowchart of the tape casting process.

water bath for 30 minute. The plasticizer/binder ratio must be adjusted to ensure that the tape was flexible, resistant and easily released from the carrier film. In this study, the plasticizer/binder ratio was designed to be 1 : 1 by weight percent. After adding the binder solution and the plasticizer, the slurries were ball milled for another 20 h. Then, the surplus solvent was evaporated and the slurry was sieved by a 300 mesh sieve. The evaporation was carried out carefully to avoid drying a skin or bubble formation. Before casting, the slurry was stirred to de-air under vacuum to remove any entrapped air bubbles. Before the de-air process, some polydimethyl siloxane fluid as a defoamer was added to the slurry. The defoamer is necessary for an aqueous system due to the high surface tension of water and its foaming tendency [12]. The slurry was maintained at $\text{pH} \approx 10$ to ensure that the slurry was well-dispersed. Tape casting was performed using a tape casting machine (LYJ-150, Beijing Orient Sun-Tec Co. Ltd., China), in which the slurries were cast onto a silicon coated polyethylene film through a blade at a speed of $3.4\text{ cm}\cdot\text{s}^{-1}$. A gap height of $350\text{ }\mu\text{m}$ was chosen. After casting, the slips were dried in air.

Characterization of the green tapes

Bulk densities of the dried tapes were determined by measuring the weight and the volume of at least seven samples ($2.5 \times 2.5\text{ cm}$) cut from the green tapes. The volume of the tapes was determined by a geometrical method, where the thickness was measured using a micrometer accurate to 0.001 mm . The samples were placed between two glass slides for thickness measurement to prevent local deformation of the tapes. The weight of the samples was measured by an electronic balance accurate to 0.1 mg .

Tensile testing of the green tapes was performed by an Instron 5848 MicroTester (Instron 5848, Instron Co., USA) with a 500 g load cell. Dumb-bell shaped

specimens with 10 mm width and 50 mm gauge length (GB 13022-91) were cut from the green tapes using a cutter. The tensile tests were performed at ambient temperature of 22 °C with a crosshead speed of 5 mm · minute⁻¹. At least ten specimens from each sample were tested.

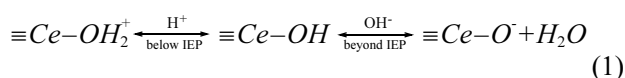
The microstructures of the green tapes were observed using a scanning electron microscope (SEM JSM-5610LV, Japan).

Results and discussion

Zeta potential

To identify the optimum pH value and dispersant content for stable slurries, zeta potentials of the SDC powder with varied dispersant contents of 1.0 wt.%, 2.0 wt.%, 3.0 wt.% (based on the SDC powder) and varied pH values were tested. As shown in Fig. 2, in the absence of the dispersant, the isoelectric point (IEP) of the SDC particles was found at pH = 3.69. In the absence of TEA, the maximum absolute zeta potential value did not exceed 35 mV, which meant that the electrostatic repulsion between the SDC particles was insufficient to stabilize suspensions if no dispersant was added. When 2.0 wt.% TEA was added, the IEP moved from pH = 3.69 to pH = 4.29, which changed for 0.60 units. And the maximum absolute zeta potential value was about 60 mV at pH ≈ 10. TEA is a dispersant with an electrostatic stabilization mechanism, which greatly influences the interaction between colloidal particles in aqueous suspensions. When dissolved in water, TEA is alkaline and electronegative due to the lone pair on its nitrogen atom. Distinct changes of surface charge in TEA-dispersed SDC suspensions were due to the adsorption of TEA on the surfaces of the particles, inducing more negative charges to the double layer. In the presence of water, most oxide

surfaces are hydrated, and for a metal oxide, there will be MOH groups on the surfaces. As illustrated in equation (1), below the IEP, adsorption of H⁺ leads to a positively charged surface, whereas beyond the IEP, adsorption of OH⁻ produces a negatively charged surface. Equation (1) can explain why zeta potentials become more positive at low pH value in the presence of TEA. As TEA can attract protons in acid solution, it makes the ≡Ce-OH surface that absorbed TEA more positively charged. As the pH value or the dispersant content increased, more negative charges adsorbed onto the SDC particles surfaces, which made the zeta potential more negative.



However, it was found that the absolute zeta potential values of the suspensions decreased with increasing pH value when pH > 10, especially when the dispersant content was larger than 2.0 wt.%. The reason is that an overfull alkalescence of the suspensions will enhance the adsorption of counterions within the Stern layer close to the SDC particle surfaces and promote the further adsorption of OH⁻ ions. This can increase the total number of charge sites, yet the net charge outside the slipping planes is reduced. Due to these two effects, the zeta potential curves showed a maximum point (absolute value) when the dispersant content was 2.0 wt.% at pH ≈ 10. Therefore, the optimum conditions for the stable dispersed slurries were 2.0 wt.% dispersant (based on the SDC powder) at pH ≈ 10.

Rheological properties of the SDC slurry

According to the zeta potential tests, TEA was employed for the stabilization of slurries with 40 wt.%, 50 wt.%, 60 wt.%, 70 wt.% solid content, and its

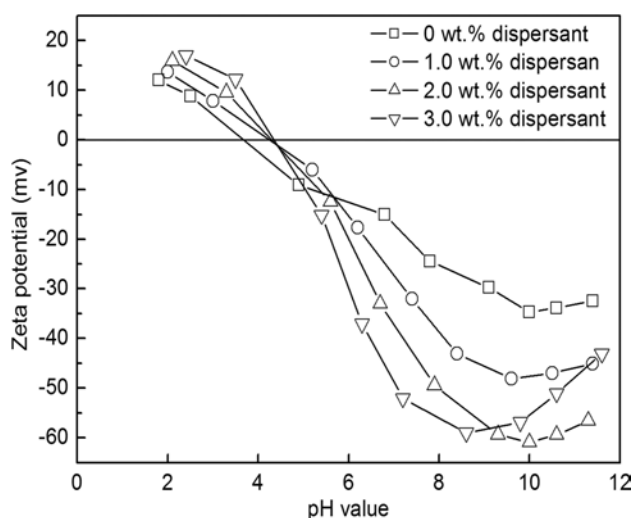


Fig. 2. Zeta potential of SDC as a function of pH after the addition of various amounts of dispersant.

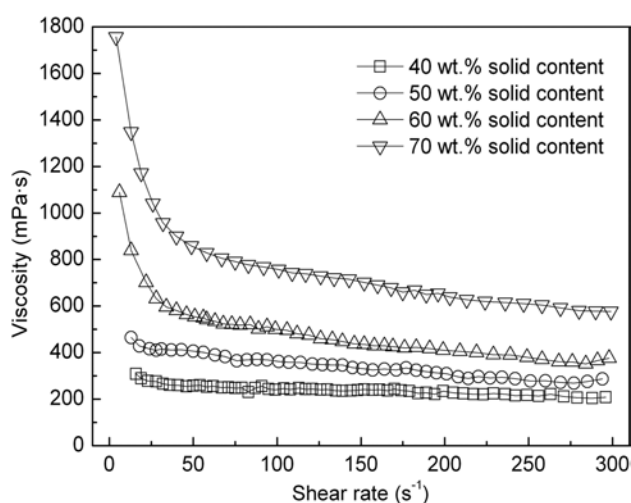


Fig. 3. Viscosities of slurries at various solid contents as a function of shear rate.

concentration was 2.0 wt.% (based on the SDC powder). The pH value of slurries was adjusted to about 10. The rheology of suspensions was greatly influenced by the solid content. The measurement results are shown in Fig. 3. The slurries with low solid contents of 40 wt.% and 50 wt.% showed a Newtonian flow behavior, although a slight shear thinning behavior was observed. The characteristic of it was a stable colloidal suspension. When the solid content was increased up to 60 wt.%, the slurries showed an obvious shear thinning behavior (pseudoplastic behavior) with a decrease in the viscosity and an increase in the shear rate. Such behavior was in good agreement with the requirements for the tape casting process because the shear stress generated by the doctor blade enabled the slurry to have a low viscosity under the blade during casting, facilitating the tape coating. When the shear stress was released, the slurry recovered a high viscosity level, avoiding settling of the particles along the tape thickness. This would preserve the homogeneous distribution of ceramic particles during the subsequent drying process. However, the slurry with 70 wt.% solid content was too viscous to cast thin tapes. The viscosity of a slurry for tape casting must be low (200–500 mPa·s) to ensure the good flowability of slurry and thinness of the tapes. So the slurry with 60 wt.% solid content was adopted.

Fig. 4 is the relationship between the viscosities of the slurry with 60 wt.% solid content and the binder content at a shear rate of 150 s^{-1} . It can be seen that the viscosities of the slurry increased with an increase in the binder content. The reason is that the active polymer can easily form cross linked structures in a water solution and adsorb onto the SDC particle surfaces driven by a non-electrostatic mechanisms such as hydrogen bonding or hydrophobic interactions [13]. As the amount of the binder increased, they could impede the relative motion of SDC particles, giving rise to an increase in the viscosities of slurries. When the binder and the plasticizer contents were both

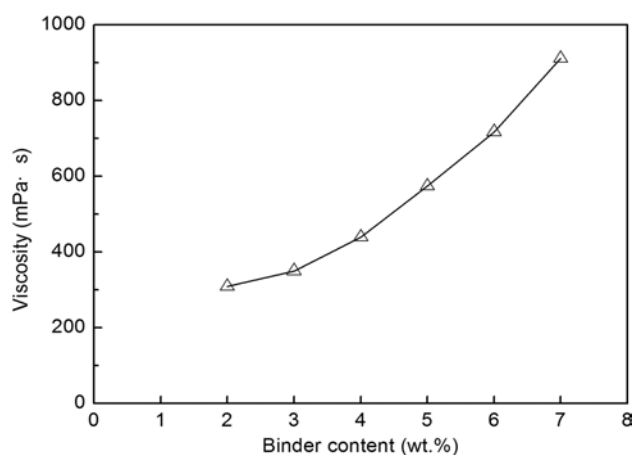


Fig. 4. Viscosities of the slurry with 60 wt.% solid content as a function of binder content at a shear rate of 150 s^{-1} .

Table 1. Composition of SDC tape casting slurry

Function	Component	Content (wt.%)
Solid	SDC	60.00
Solvent	Distilled water	30.70
Dispersant	TEA	1.20
Binder	PVA	4.00
Plasticizer	Glycerol	4.00
Deformer	Polydimethyl siloxane fluid	0.10

4 wt.%, the viscosity was suitable for tape casting. If the contents were more than 4 wt.%, the slurries were too viscous to cast thin tapes. And a larger amount of polymer would lead to a higher porosity after burning-out of the organic components. If the contents were less than 4 wt.%, not only was a high dispersion of slurry difficult to ensure because the powder in a low viscosity slurry sedimentated more easily than that in high viscosity slurry, but also green tapes with a low mechanical strength would appear. So the slurry with 60 wt.% solid (the SDC powder), 4 wt.% binder and 4 wt.% plasticizer contents was adopted. The optimum composition of the tape casting slurry is shown in Table 1.

Tape casting and drying

The wetting behavior of the substrate film by the aqueous SDC slurry is important. A serious de-wetting problem is met with a coated substrate film. The reason is that water has a rather high surface tension in comparison with organic solvents. In this study, TEA was used as the dispersant, which also played a role of an excellent surfactant. The high surface tension $0.073 \text{ N} \cdot \text{m}^{-1}$ of water can be reduced to $0.040 \text{ N} \cdot \text{m}^{-1}$ by adding 1 wt.% of TEA [14]. This led to acceptable wetting in combination with the easiness of detaching and winding the tapes from the substrate film (seen in

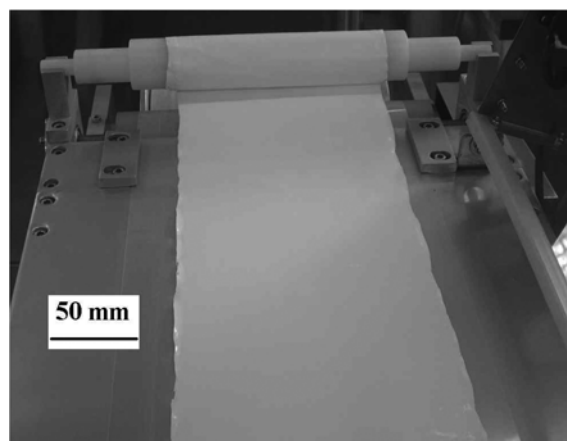


Fig. 5. Winding of SDC green tape detaching from the substrate film.

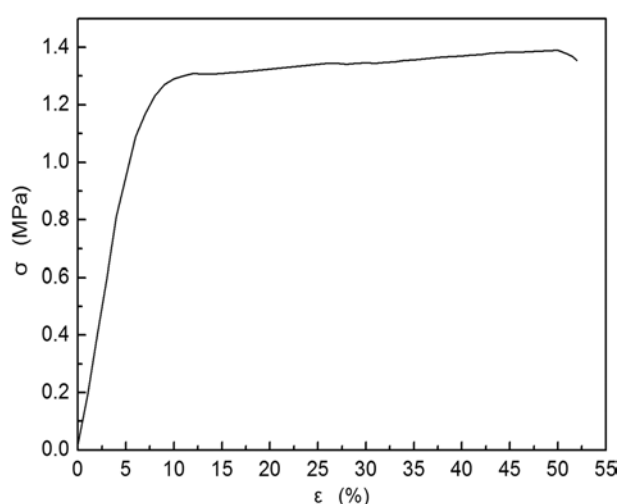


Fig. 6 Stress-strain curve of the green tape with 60 wt.% solid content.

Fig. 5).

During the drying process, the aqueous phase evaporated and the polymer shrank and compacted to form a tape. Glycerol was used to increase the flexibility and workability of the tapes. However, the addition of a plasticizer tended to reduce the strength of green tapes. It has been reported that the tensile strength would decrease linearly with the increasing plasticizer content [15]. And the tapes with a higher strength showed a lower strain to failure. So the content of plasticizer should be properly adjusted to optimize both the tensile strength and flexibility of the green tapes. In this study, the content of glycerol in SDC slurries was the same as that of PVA by weight percent. Fig. 6 shows a typical tensile curve of the green tape with 60 wt.% solid content. It can be seen that the tape exhibited good ductile behavior. The maximum stress reached 1.39 MPa and the strain to failure was about 52%. The results showed that the SDC green tape with the same content of the binder and the plasticizer not only had a satisfactory strength but also a high plasticity.

After drying at 25 °C for 36 h and then 40 °C for 6 h in air, the dried tape with a thickness of 150 μm was smooth, defect-free and flexible (seen in Fig. 5). The average green density of the dried tape was about 56.9%. This high green density was probably ascribed to the high solid content of the SDC suspension. The microstructure of the SDC green tape is shown in Fig. 7. It can be seen that both sides of the tape (top surface in contact with air and bottom surface) exhibited bright and smooth surfaces. The particle packing in the tape was homogeneous. The cross section of the green tape was also homogeneous and no density gradient was observed. This was due to the fact that the SDC suspension was well-dispersed and the slurry exhibited an obvious shear thinning behavior as mentioned before.

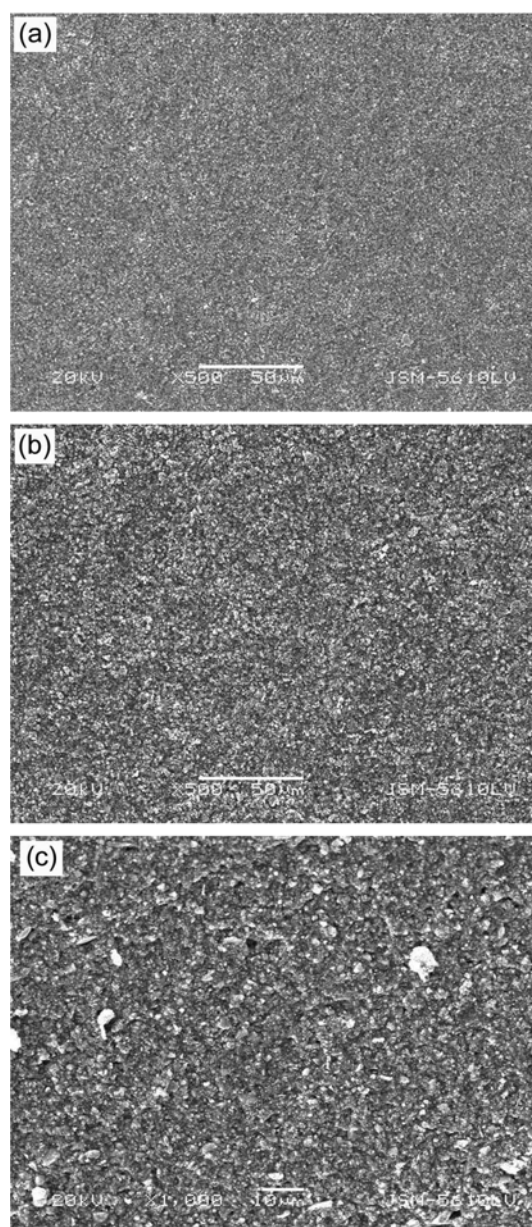


Fig. 7 SEM micrographs of the dried tape: (a) top surface in contact with air; (b) bottom surface; (c) cross section.

Conclusions

The use of TEA as a dispersant not only increased the zeta potential absolute values of the SDC suspensions, which resulted in a good dispersion of the SDC suspensions, but also led to an easiness of detaching the tapes from the substrate film. In the presence of 2.0 wt.% (based on the SDC powder) TEA, the IEP of SDC shifted from pH = 3.69 to pH = 4.29, and the maximum absolute zeta potential value increased from 35 mV to 60 mV. The pH value also greatly affected the stability of the SDC suspensions. The optimum pH value of the SDC suspension was found to be about 10. The aqueous slurry with 60 wt.% SDC, 1.2 wt.% TEA, 4 wt.% PVA and 4 wt.% glycerol

contents showed an obvious shear thinning behavior and a suitable viscosity at a pH of about 10, which was fit for the tape casting process.

TEA dispersant and PVA binder were pre-dissolved and added in a dilute stage to guarantee a homogeneous distribution of the slurry. Polydimethyl siloxane fluid was used as a deformer. After drying at 25 °C for 36 h followed by 40 °C for 6 h in air, flexible, homogeneous, defect-free and smooth SDC tape with a thickness of 150 µm was successfully produced via an aqueous tape casting process.

The ultimate tensile strength of the green tape with the same content of binder and plasticizer reached 1.39 MPa and the strain to failure was about 52%. The high solid content (60 wt.%) of the SDC slurry enabled the production of a homogeneous green tape with a high green density of 56.9%.

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