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Preparation of Na-beta″-alumina film by tape casting process

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Abstract

This study focused on the preparation of Na-beta″-alumina film by a tape casting process. The effects of solvent, dispersant, binder, plasticizer contents, as well as milling time on the rheological properties of the slurry were investigated. The dispersion of the ceramic powder in the slurry was optimized by ball milling an azeotropic mixture of methyethylketone (MEK) and ethanol (EtOH) as the solvent, 2 wt% triethanolamine as the dispersant, 7 wt% PVB as the binder for 4 h. Green Na-beta″-alumina thick films with thickness of 100–300 μm and homogeneous microstructure were obtained and further sintered at 1600 °C to obtain a relatively dense membrane with a thickness of ca. 100 μm. The conductivity of the sintered ceramic was comparable to that obtained by the conventional isostatic pressing and sintering method.

Keywords: Tape casting; Ionic conductivity; Microstructure-prefiring; Na-beta-alumina; Batteries

1. Introduction

The fast-ionic conductor Na-beta″-alumina has been confirmed as a useful material in many applications, such as sodium sulfur battery, alkali metal thermoelectric converters, sodium sensors and electrochromic displays.[1] The high conductivity makes Na-beta″-alumina one of the best solid electrolytes known up to now.[2] As known, the resistance of an electrolyte is inversely proportional to the thickness of the electrolyte separator. In order to realize a low resistance, it is necessary to reduce the thickness of the electrolyte. Fabrication of a thick Na-beta″-alumina film represents a high difficulty. A lot of methods have been developed for the preparation of the Na-beta″-alumina film, such as slip casting, extrusion, isostatic pressing, electrophoretic forming, followed by sintering.[3] Yoldas and Partlow prepared the thin film from metal-organic-based precursor solutions by a sol–gel method at a relatively low temperature.[4] More recently, Kim et al. have fabricated Na-beta″-alumina films by thermal plasma processing.[5]

However, the mentioned methods displayed some disadvantages, such as high cost, complicated equipments and unsuitability for large-scale production. Compared with these methods, tape casting is a cost-effective ceramic forming technique that can be applied to produce green thick films with homogeneous microstructure, smooth surface and precise dimensional tolerance. Moreover, it is suitable for large-scale production. Some reports mentioned the fabrication of beta alumina by this technique.[6]

The aim of this paper was to fabricate Na-beta″-alumina ceramic films by tape casting technique. The influence of the slip additives and the solvent systems on the rheology of the slurry was systematically studied.

2. Experimental

2.1. Preparation of Na-beta″-alumina powders

In this work, the purity grade of the reagents was AR and the chemicals were commercially obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd. According to a previous report,[7] a two-step-synthesis procedure was applied to prepare the beta″-alumina powder. Firstly, two kinds of precursors of $NaAl_5O_8$ and $LiAl_5O_8$, nominated as Na-zeta and Li-zeta, respectively, were fabricated by a solid state reaction at 1250 °C for 2 h. Then the $NaAl_5O_8$ and $LiAl_5O_8$ precursors were further mixed together by ball milling for 4 h. The ratio of $NaAl_5O_8$ to $LiAl_5O_8$ was determined according to the chemical formula of beta″-alumina as $Na_{1.67}Al_{10.67}Li_{0.33}O_{17}$. The mixture was used as the raw material of the slurry for the tape casting. Fig. 1 shows the morphology of the dried mixture. A slice-like shape was

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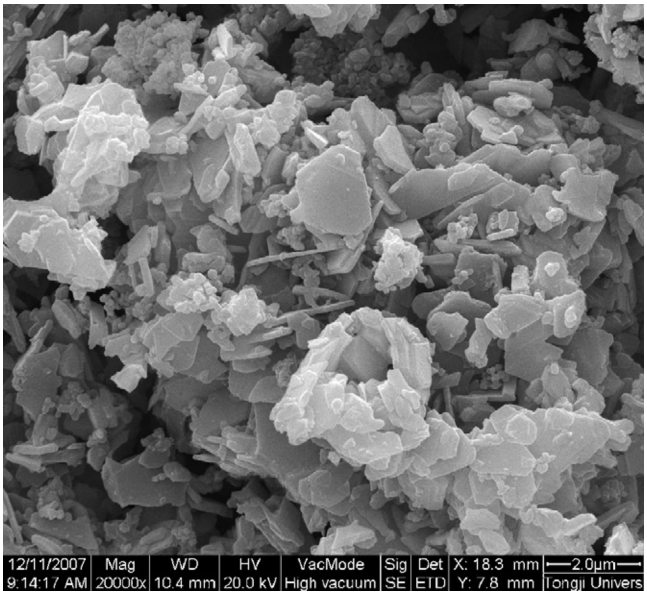

Fig. 1. Microstructure of the mixed powder.

observed for the particles of the precursor powder. The mean particle size was 1.26 μm as measured by a JL-1177 laser particle size analyzer.

2.2. Preparation of slips and casting of green tapes

The preparation of the slip was performed by considering the effect of the adding order of the slurry additives.[8,9] In order to avoid competitive adsorption, the slurry was prepared by a two-step mixing procedure. Firstly, the powder, the solvent and the dispersant were mixed together. Then the polymer binder and plasticizer were added to the mixture. In all cases, a planetary ball milling with nylon jar and zirconium balls were used. The slurry was homogenized by ball milling for 12 h at a very low speed of 40 rpm, which was an effective way to remove the air contained in the slurry.[10]

It is well known that in the tape casting process, the support or carrier sheet are of prime importance, because the wetting ability of the slurry with the support is essential for a good adherence. However, strong adherence between the support and the dried tape results in difficulty in stripping the tape from the support. Mylar film, glass coated with silicon oil and polyethylene sheet have been selected as a possible support for different material systems.[11,12] However, they are unsuitable for beta″-alumina because the strong adhesion between the dry tape and the support. In the present investigation, the stainless steel was investigated as the support. As found, it was very easy to release the tape from the support. This could be due to the large difference of the surface tension between the tape and the stainless steel sheet, which reduces the adhesion joint after drying. Casting process was performed in a self-made machine with a stationary carrier and a doctor blade moved at a controlled speed. The slip passed through a blade system to ensure a uniform thickness of the tape. The height of the doctor blade can be adjusted by means of micrometer screws.

The cast tape was dried at room temperature for about 24 h. In order to avoid the crack of the tape because of the fast evaporation of the solvent,[13] an organic glass box was used. The removal of the organic contents in the tape, the sintering and the phase transformation of the ceramic powders were processed by further heat treatment. In order to avoid the evaporation of sodium content at high temperature, the green bodies were embedded inside the raw powders with the same compositions as those of the green bodies during the sintering process.[14]

2.3. Characterization

The crystalline phases corresponding to the Li-zeta, Na-zeta and beta″-alumina ceramics were confirmed by X-ray diffraction analysis (Rigaku RAD-C, 12 kW) at room temperature using Cu Kα radiation in the 2θ range from 5° to 80°.

The rheological behavior of the slurry was measured using a Brookfield viscometer (Model RDF, Spindle No. 5, and speed factor 2) at a constant temperature of 25 °C.

The cast tape was characterized in terms of bulk density as well as the microstructure of the green tape. The bulk density was measured by the Archimedes method using water as the immersing media.

In order to observe the packing state of the raw particles in the tape, the microstructure of the tape was studied using a scanning electron microscope (FESEM, JEOL, JSM-6700F) after the burnout of the binder and other organic additives.

Polished samples were prepared for ionic conductivity measurements with gold electrodes sputtered on both sides of the samples as the blocking electrodes. The four-probe impedance measurements of the sintered ceramics were carried out on a Solartron 1260 impedance analyzer over the frequency range of $1–10^6$ Hz.

3. Results and discussion

3.1. Effect of the solvent

The selection of an appropriate solvent was imperative for the preparation of the slip. The dispersion of ceramic powder in several non-aqueous systems, including methyethylketone/ethanol (MEK/EtOH), trichloroethylene/propyl alcohol, ethanol and cyclohexanone, was evaluated for tape casting. The former two systems consisted of azeotropic mixtures in order to avoid differential evaporation. Table 1 shows the main characteristics of the solvents used in this work. Fig. 2 shows the rheological curves for ceramic slurries in different solvent systems with solid loading of 15 vol.% (a and b) and solid loading of 22 vol.% (c and d), respectively.

It can be seen from the rheological curves shown in Fig. 2 that the entire slips display shear thinning behavior, which can be monitored by an estimation of the flow index obtained from the following empirical power law equation[15]:

$$\boldsymbol{\tau} = \boldsymbol{k}\gamma^n \tag{1}$$

where $\boldsymbol{\tau}$ is the shear stress, γ the shear rate, $\boldsymbol{k}$ a consistency factor and n the pseudoplasticity index. For pseudoplastic suspensions,

Table 1
Main properties of the organic solvents considered in this work.

Solvent	Evaporation rate (aether = 1)	Dielectric constant	Viscosity (mPa s, 25 °C)	Surface tension ($\times 10^3$ N/m, 25 °C)
EtOH	8.3	24	1.2	22.27
MEK	3.1	18	0.4	24.6
TCE	0.28	3	0.4	25
Propyl alcohol	–	18	2.4	22
Cyclohexanone	40	18	0.8	35

the value of n is less than 1. The shear thinning behavior is caused by the alignment of binder molecules at high shear rate. This behavior is advantageous for the tape casting process because the viscosity of such slip decreases when the slip passes through the casting blade. After passing through the blade, no shear force appeared and the viscosity of the slip increased again. The fast recovery to high viscosity preserved the homogenous structure of the slip by reducing the mobility of its constituents[16].

It is obvious from Fig. 2(a) and (b) that with the solid loading of 15 vol.%, the viscosity and shear stress in different solvent system have a following order:

EtOH < EtOH/MEK < trichloroethylene/propyl alcohol
< cyclohexanone

The slip prepared in EtOH and azeotropic mixture of MEK and EtOH had almost the same viscosity. When the solid loading increased to 22 vol.%, as shown in Fig. 2(c) and (d), the order changed to be:

EtOH/MEK < EtOH < trichloroethylene/propyl alcohol

It was found that the slip prepared in cyclohexanone lost flowability and much PVB agglomeration existed. Therefore the rheological properties of the slip cannot be measured.

As known, the viscosity of the slurry is mainly affected by the solvent and binder used. The surface tension and the functional groups of the molecular play the key roles. Lower surface tension is preferable to obtain a better wetting of the powder. If a solvent and a binder have the same functional groups, they may exhibit

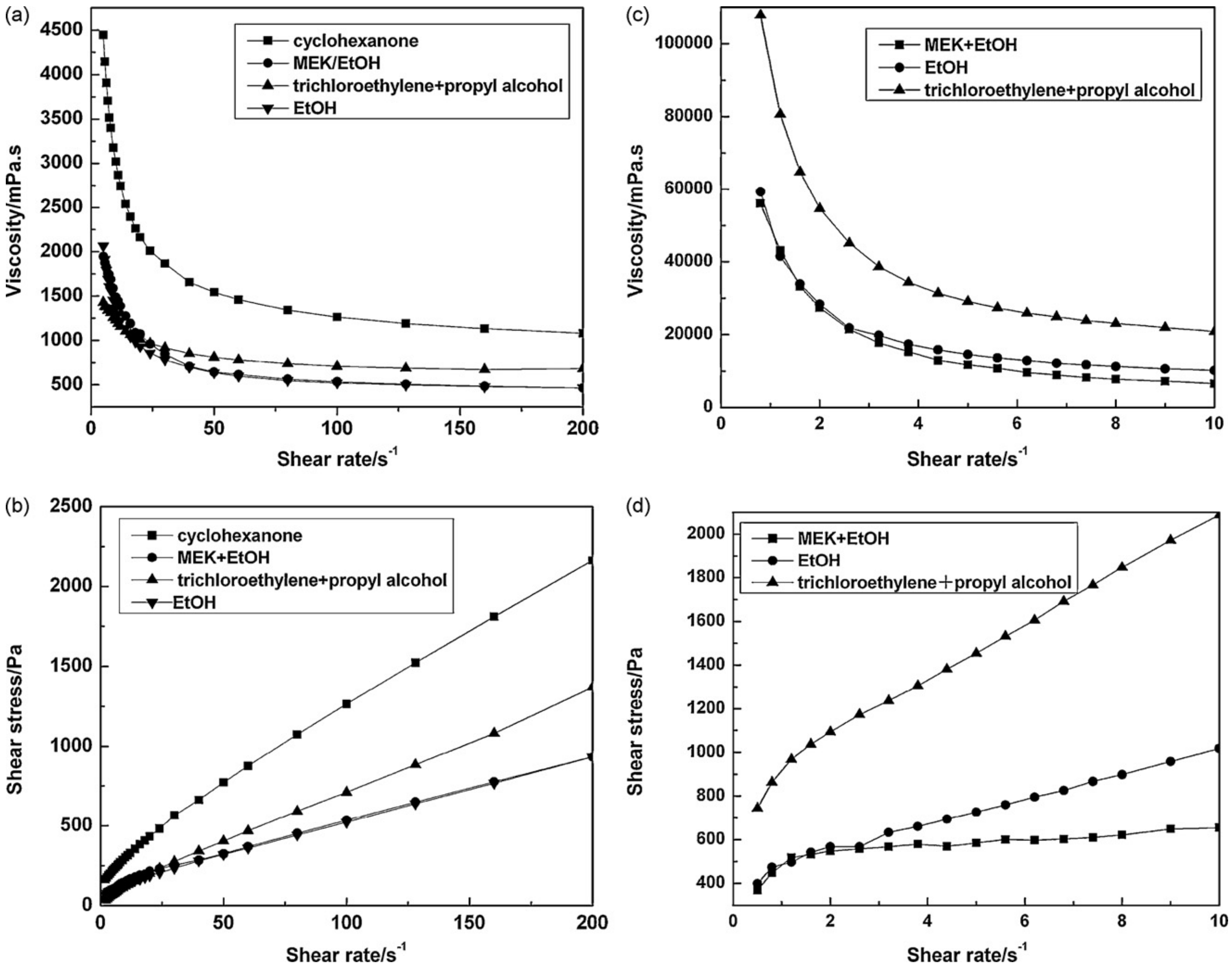

Fig. 2. Rheological curves for ceramic slurries in different solvent systems with solid loading of 15 vol.% (a and b) and solid loading of 22 vol.% (c and d), respectively.

similar polarity or form hydrogen bond between their molecules, which promotes the dissolution of the binder in the solvent and decreases the viscosity of the slip system.

For the slurry with lower solid loading, the surface tension of the solvent plays a leading role. The surface tension of the solvents used has the following order:

$$\text{propyl alcohol} < \text{EtOH} < \text{MEK} < \text{trichloroethylene} < \text{cyclohexanone}$$

That is to say, EtOH is the most favorable solvent for the wetting of the powders. This can well explain the fact that the slip prepared in EtOH with the solid loading of 15 vol.% had the lowest viscosity.

On the other hand, for the slurry with higher solid loading, low surface tension of the solvent and high solubility of the binders with the solvent are essential, since high solid loading generally results in an increased amount of the organic additives. MEK and EtOH have the one or two same functional groups, such as –OH and –C=O, which are similar with those of the PVB.[17] These functional groups promote the dissolution of the PVB. Thus the slip with solid loading of 22 vol.% using EtOH/MEK as solvent had the lowest viscosity.

The evaporation rate is another important characteristic. To obtain thick tapes (100–300 μm), a volatile solvent was favorable to reduce the drying time.[17] Here, EtOH/MEK azeotropic solvent is suitable for the drying process.

It has been shown that a better degree of dispersion gives a higher stability of the suspension and a lower viscosity. Thus the viscosity of the slip should be as low as possible to ensure the slurry a favorable flowability. According to the results above, azeotropic mixture of MEK and EtOH was selected as a proper solvent.

3.2. *Effect of the dispersant concentration*

Dispersant plays a critical role in stabilizing the slurry. Different kinds of dispersants have been tested. Glycerol trioleate based dispersant, a kind of zwitterionic dispersant, has been successfully used in many ceramic powder slurries.[18] However, it has almost no dispersing effect for the Na-beta″-alumina-based slurry. On the other hand, the dispersion of ceramic powder in non-aqueous system was studied with triethanolamine, a kind of non-ionic dispersant.[19] Although its carbon chains are not long enough to provide steric potential energy barriers, triethanolamine can allow stabilization by an adsorption onto the surface of the powder. The stabilization acts by reducing the London–Van der Waals attraction among the ceramic particles. This action has been termed as semisteric stabilization and is successfully applied for many ceramic slips. It is also effective for beta″-alumina slurry. In this work, triethanolamine was selected as the dispersant.

In order to determine the optimum dispersant content, viscosity values as a function of dispersant concentration varying from 0.025 wt% to 4 wt% with respect to the ceramic powder were studied and shown in Fig. 3. It is obvious that triethanolamine is effective to disperse the Na-beta″-alumina powders. It can prevent the agglomeration of the powder at a concentration of about 2 wt%, at which the minimum viscosity was reached.

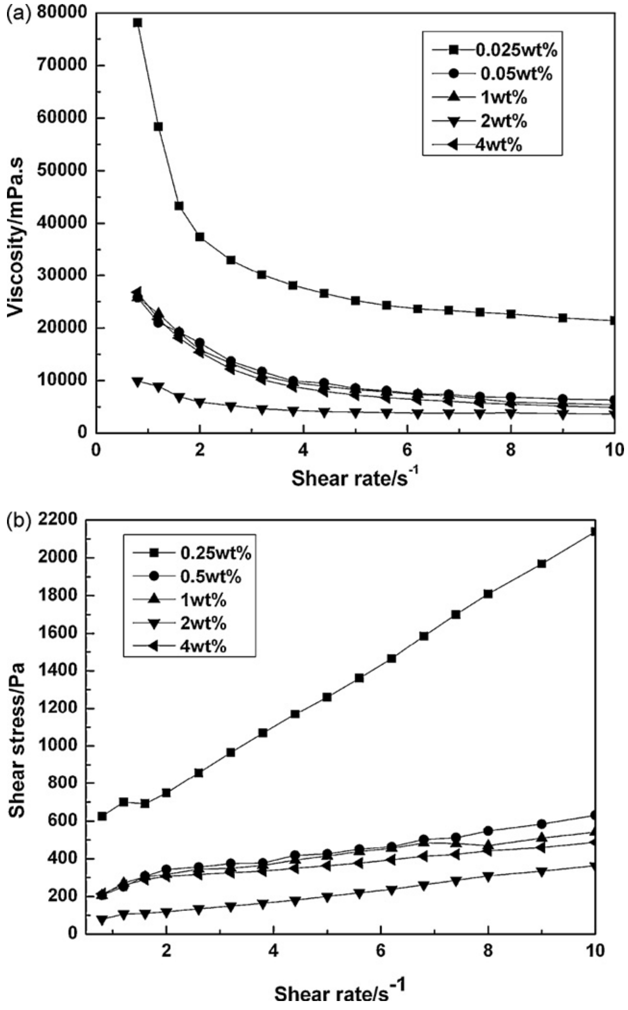

Fig. 3. Variation of slurry viscosity and shear stress with dispersant concentration.

3.3. *Effect of binder and plasticizer on the slurry rheology*

One of the most important roles of the polymer binder is to provide the tape with a sufficient strength. In this study, poly-vinyl-butyl (PVB) powder was used as the binder and polyethylene glycol (PEG200) liquid was selected as the plasticizer.

As found, the binder content less than 6 wt% with respect to the ceramic powder could not provide the green tape with a sufficient strength to support the post handling, whereas the binder content over 10 wt% led to high viscosity of the slurry and made it much difficult to obtain a homogeneous mixture. Therefore, the concentration of the polymer binder was chosen in the range from 6 wt% to 9 wt% with respect to the ceramic powder. Furthermore, the weight ratio of binder to plasticizer was fixed at 1:1.5.[18]

The further optimization of the binder content was based on the characterization of the green tape density. Table 2 lists the green density of the tape. It was seen that the tape had the highest

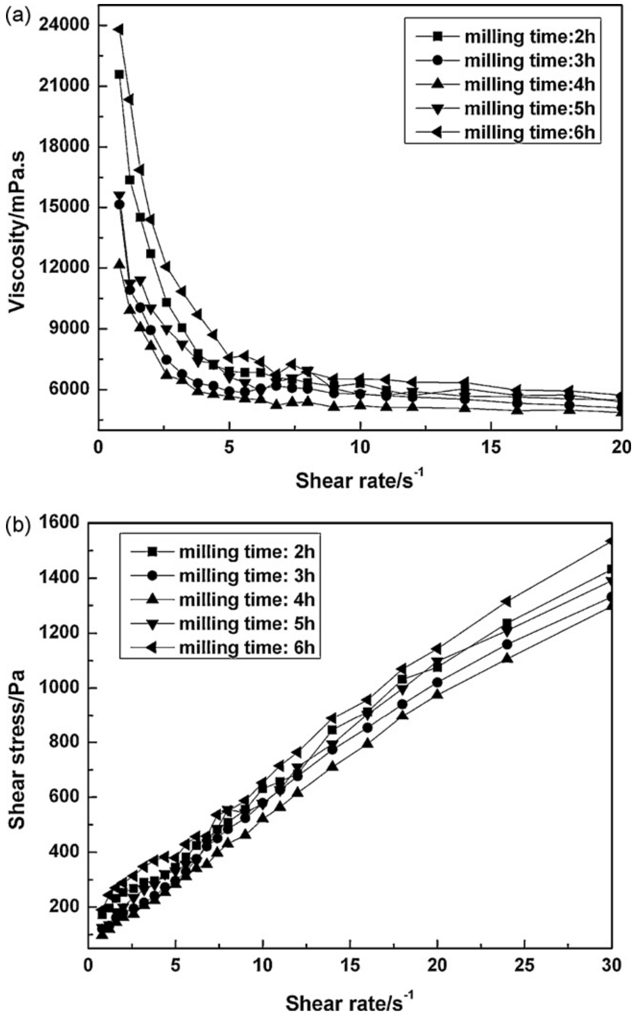

Fig. 4. Effect of milling time on the rheological curves of slurries.

bulk density as the content of the binder accounted 7 wt% of the ceramic powder.

Excessive amount of the organic components generally results in a severe inhomogeneity of the slurry and leaves many pores after the burnout stage. It is disadvantageous to the densification of the ceramics. The binder content was thus chosen at 7 wt% by achieving a balance between the quality of tape suitable for handling and the efficiency of the burnout of the organic additives.

3.4. Effect of the milling time

The addition of the binder increased the viscosity of the slurry. This could be greatly alleviated by completely dissolving the binder. Ball milling provides a useful process and the selection of an appropriate milling time can effectively promote the dis-

Table 2
Bulk density with different binder amounts.

PVB content	6 wt%	7 wt%	8 wt%	9 wt%
Bulk density (g/cm^3)	1.489	1.697	1.441	1.546

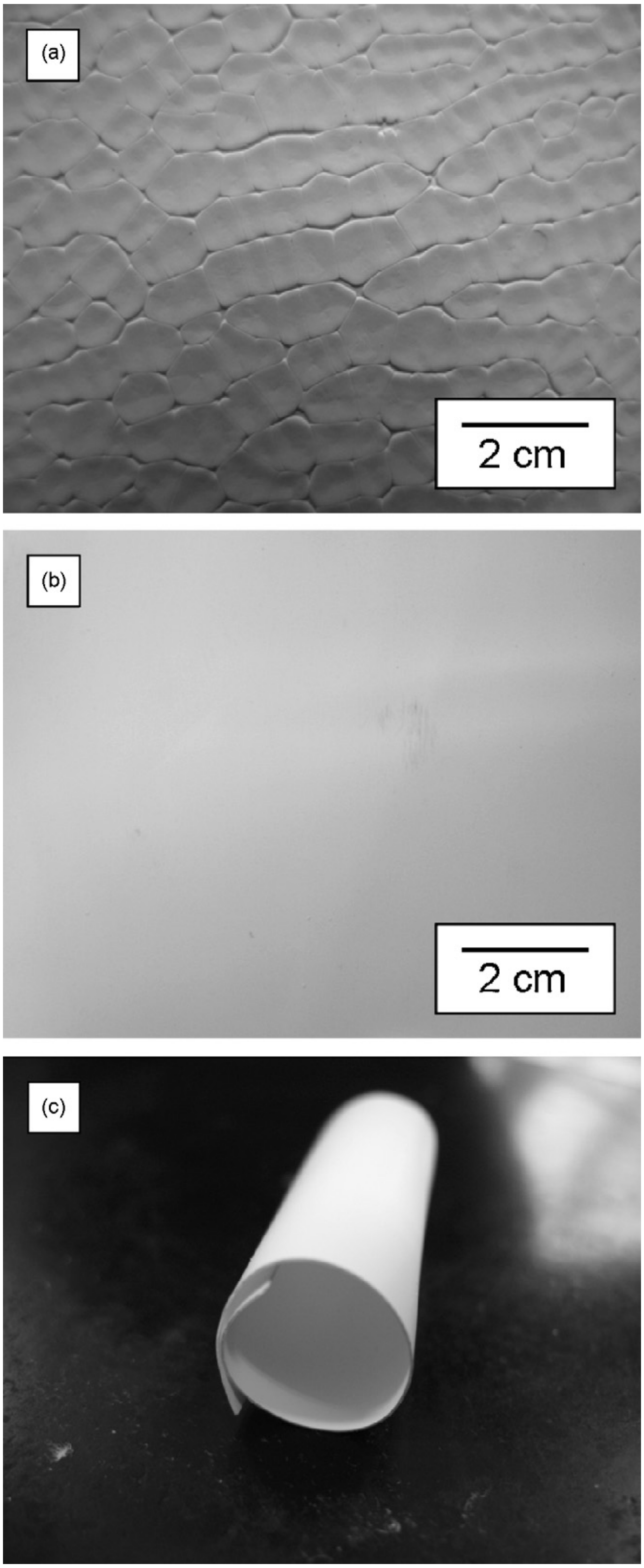

Fig. 5. Photographs of (a) the surface cracks on cast tape with the solid loading lower than 15 vol.%, (b) surface of the dried tape with solid loading of 22 vol.% (c) the as-prepared beta-aluminum thick film.

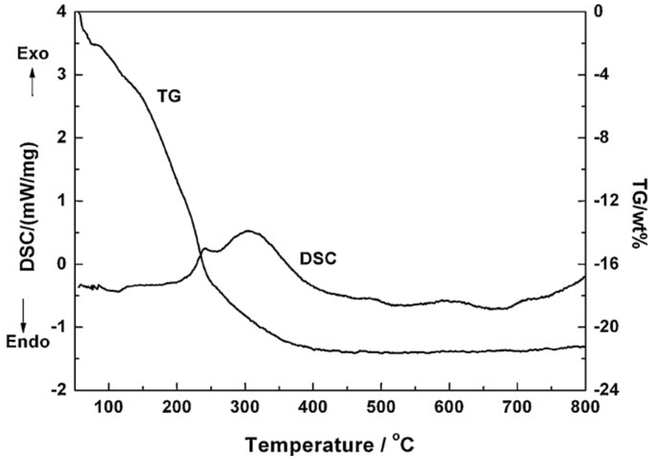

Fig. 6. TG/DTA curves of green tapes.

solution of the binder. As found, a too long milling time could damage the binder molecules and resulted in a degradation of the tape strength. In contrary, the binder could not be dissolved completely if the milling time was too short.

Fig. 4 shows the effect of milling time on the slurry rheology. The slurry rheology decreased at the beginning and increased with milling time from 2 h to 6 h. It was found that the slurry turned to be very sticky if the milling time was prolonged to 12 h. On the contrary, PVB agglomeration existed in slurry when the milling time was shorter than 1 h. The lowest viscosity was obtained when the milling time was 4 h.

3.5. Microstructural and electrical characterization

The appearance of the tape was found to be very sensitive to the content of solid loading. When the solid loading was lower than 15 vol.%, all tapes showed cracks, regardless of the binder amount, as shown in Fig. 5(a). However, much higher content of the binder might be introduced as the solid loading was higher than 25 vol.%. This resulted in a severe agglomeration of the slurry. Based on the experiment, the optimum solid loading was determined as 22 vol.%. Fig. 5(b) shows the smooth surface of the dried tape with the solid loading of 22 vol.%. The photograph shown in Fig. 5(c) indicated that the as-prepared green film has a good flexibility. The thickness of the film was measured to be 100–300 μm, which is much thinner than that obtained by conventional method, such as isostatic pressing.

In order to observe how the precursor particle packed in the green tape, the green tape was pre-sintered to remove the organic additive. DT/TGA curves shown in Fig. 6 revealed that two exothermic peaks appeared at around 243 °C and around 303 °C respectively, which mainly resulted from the decomposition of the binder and the removal of the organic components. Accordingly, the green tape was burned out at about 400 °C for 2 h.

Fig. 7(a) and (b) shows the scanning electron micrographs of upper surface and undersurface of a tape after burned out, respectively. No obvious heterogeneity or difference on the morphology was observed between the upper surface and under-

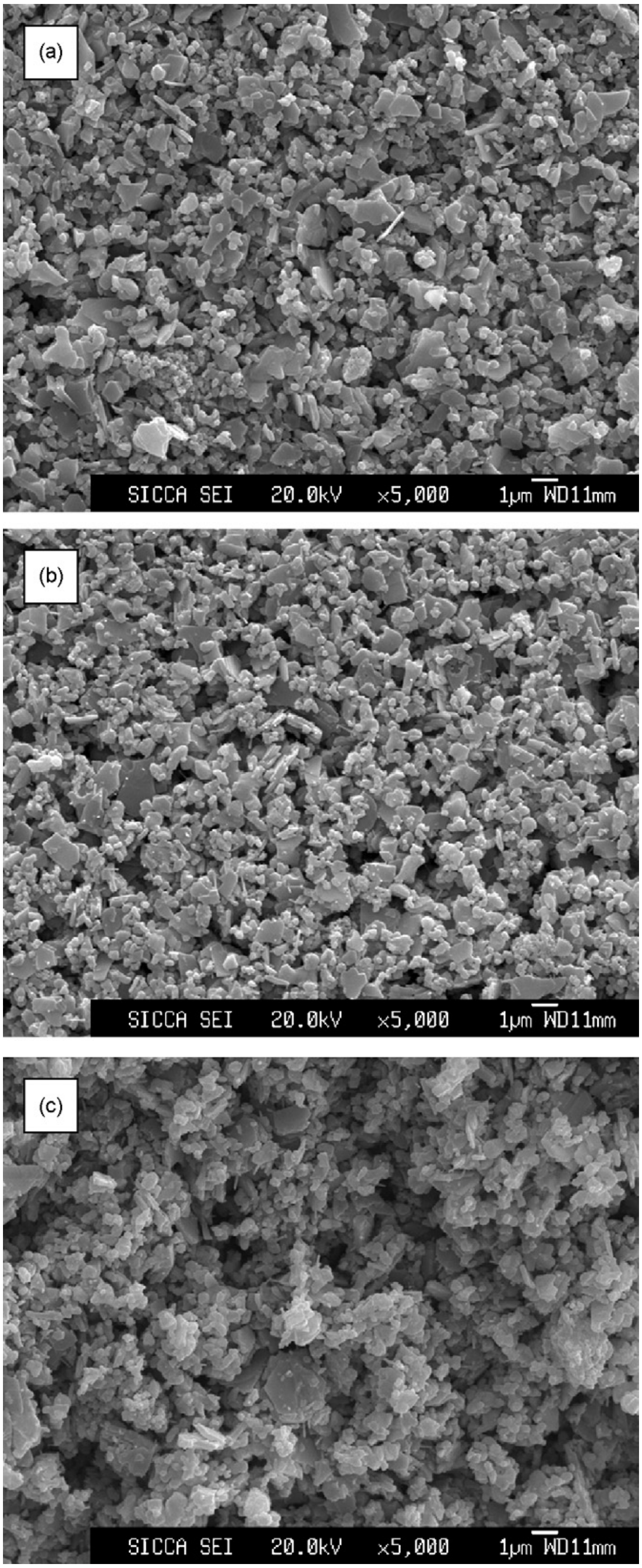

Fig. 7. Microstructure of the burned tape with solid loading of 22 vol.%: (a) upper surface, (b) undersurface, and (c) cross-section.

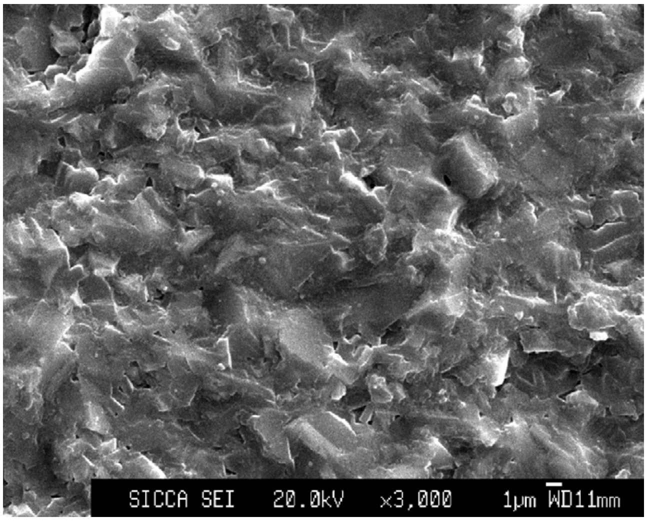

Fig. 8. Microstructure of the fractured cross-section of the sintered tape from the green tape with solid loading of 22 vol.%.

surface, suggesting that the as-prepared tape was homogeneous. No significant agglomeration of the ceramic particles though burned green bodies was found, as shown in Fig. 7(c). It was demonstrated that the as-optimized technique conditions were suitable for the preparation of the thick green film of the Na-beta″-alumina-based slip.

Fig. 8 shows the SEM microstructure of the fractured cross-section of the Na-beta″-alumina ceramics sintered at 1600 °C for 10 min. No obvious pore or crack through the ceramic was observed. The sintered ceramics reached a relative density of 97% T.D. The thickness of the as-sintered film was approximately 100 μm. Such a thickness was obviously thinner than that obtained by a conventional isostatic pressing and sintering.[3]

The ionic conductivity of the ceramics at 200 °C was obtained as 0.012 S cm^{-1}, which was comparable to the conductivity of the film obtained by the isostatic pressing and sintering.[7]

4. Conclusions

In this work, the Na-beta″-alumina green tape was obtained by a non-aqueous tape casting process. The concentration and the nature of the dispersant, the binder and the plasticizer were optimized in terms of the rheological behaviors and the characteristics of the green tape. Regarding to the slip, the best dispersion was achieved using an azeotropic mixture of MEK and EtOH as the solvent, 2 wt% triethanolamine as dispersant and 4 h of the milling time for the binder. The optimum content of the binder was 7 wt%. The green tape prepared by casting the slurry had a uniform microstructure. After sintering at 1600 °C, the relative density of the ceramics with a thickness of 100 μm was 97% T.D. The ionic conductivity of 0.012 S cm^{-1} for the ceramics was reached at 200 °C. The conductivity was comparable to that obtained by the conventional isostatic pressing and sintering method.

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