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Tape Casting of anode and electrolyte layers for solid oxide fuel cells

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This work describes a technology of obtaining an anode and electrolyte layers of SOFC by Tape Casting method. The optimal suspension composition and casting conditions were established and explained by analysis of suspension`s nature of the flow and amount of stresses which it receives during casting. Typical defects were identified and methods to avoid them were suggested. Advantages of step-by-step lamination were demonstrated.

Keywords: *tape casting, solid oxide fuel cells, anode, electrolyte, suspensions, rheology, tape defects.*

Introduction

Tape casting is an important technology, which allows an obtaining of thin elastic tapes with high density, a predetermined thickness and a uniform distribution of powder in a volume of the tape. By using a not complicated equipment this technology provides obtaining of thin tapes from all materials in a powder state. The method is widely used as a basis for the manufacturing of all modern electronics and constantly upgrades. Creation of ceramic films by the Tape Casting method for later use in the solid oxide fuel cell (SOFC) is an important task because of the high performance, low cost and environmentally friendly of this method. However, to obtain high-quality films some technical and scientific problems needs to be solved. The tapes must have different thickness and porosity with equable powder distribution by volume and be a defect-free with low surface roughness. The influence of casting conditions and rheological behavior of suspension on tapes properties must be studied deeply in order to predict these properties before casting. Traditional approaches to determining the influence of casting conditions on tape properties should be reviewed and supplemented by taking into account rheological parameters such as shear rate and shear stress. Particular attention should be paid to the mechanisms of defects formation in tapes and the methods of avoiding must be suggested. More attention must be paid to the analysis of the technology of multilayer ceramic packages assembling because the SOFC lifetime depends on the package's integrity.

The objects and methodology of the experiment

The 8YSZ (Zirconia Ukraine Ltd., Ukraine) and NiO (“Metals Kingdom Industry Limited”, China) powders were used as a solid phase of tapes. The polyvinyl butyral (PVB) was used as the binder, 1-n-butanol and isopropyl alcohol as solvents and dibutyl phthalate (DBP) as a plasticizer.

Preparation of suspensions was carried out in two stages. In the first stage, an organic binder solution was prepared by dissolving polymer of polyvinyl butyral (PVB) in two types of organic solvents: butanol and isopropyl alcohol using a magnetic stirrer RCT basic of ICA. After dissolving the polymer, a plasticizer (DBP) was added to the solution. In the second step, the powder was mixed with the binder solution and homogenized in a ball mill for 24 hours.

A laboratory TTC-1200 casting machine equipped with an aluminum doctor blade was used for casting. The height of a blade is regulated by two microscrews and can be adjusted from zero to a few centimeters with accuracy regulation of 10 microns. Substrate speed varies from 1 to 55 cm/min. The Mylar polymer film with antiadhesive silicon coating was used as the substrate. A rotational viscometer Medingen «Rheotest RN4.1» was used for rheological analysis of the suspensions. The creation of a package of green fuel cell layers was carried out using the Jumbo 30 vacuum packing machine. The isostatic pressing of the package in water provided by isostatic laminator IL-4008 PC (with a maximum pressure of 8000 psi, corresponding to 55 MPa) with the possibility of heating the sample to 80 °C. VMK1600 ("Linn High Term", Germany) furnace was used to sinter assembled package.

Results and discussion

A various suspensions compositions suitable for further casting and processing into a fuel cell was prepared and compared (table 1). Was obtained a porous anode tapes with a thickness of 100 to 400 microns from a mixture of 8YSZ and NiO powders, high-density electrolyte tapes with a thickness of from 50 to 150 microns based on 8YSZ powders and tapes of contact layer with a thickness of about 70 microns based on NiO powders.

An important task is to the determinate influence of casting conditions on tapes properties. This study helps predict a tape thickness before casting.

Influence of casting conditions on tapes properties. During the tape casting process, a suspension is affected by mechanical stress caused by two main casting parameters: a blade gap height and carrier speed. These two parameters can be represented by shear rate value. The theoretical value of simple shear rate can be calculated by dividing a speed of carrier to a blade gap height (table 2).

Using a shear rate to tape thickness dependence instead of the traditional approach [1] with blade gap and carrier speed to tape thickness dependence helps in comparison and characterization different suspensions, which do not vary much in viscosity.

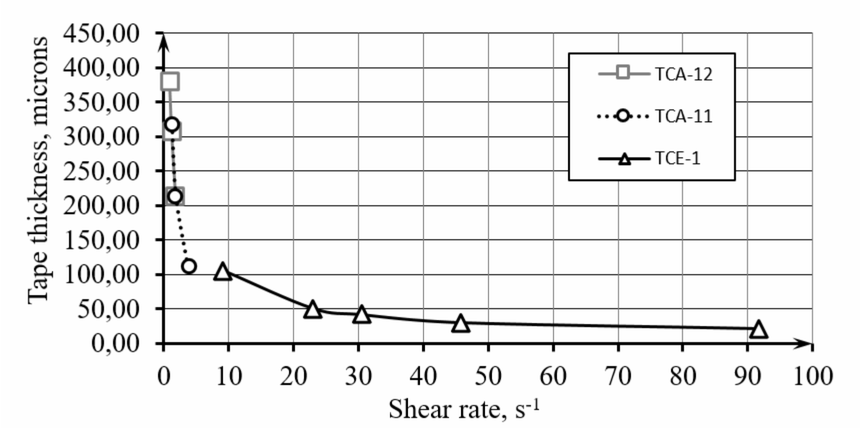
This dependence shows that great contribution in a tape thickness casting condition made in a range of low shear rate. But when mechanical stress increases greatly a tape thickness dependence becomes almost linear (fig. 1).

Table 1. Suspension compositions

Layer type	Powder type	Component content, % (mass.)			
		Powder	Binder	Solvent	Plasticizer
Electrolyte	8YSZ	48	4	46	2
Anode	8YSZ and NiO	48	4	46	2
NiO layer	NiO	38	5	54	3

Table 2. Casting conditions and tapes properties

Tape name	Blade gap height, microns	Carrier speed, m/min	Average tape thickness, microns	Viscosity (under shear rate 4 s^{-1}), mPa·s	Casting shear rate, s^{-1}	Viscosity (under casting shear rate), mPa·s
TCE-1	100	0,55	21	9210	91,67	—
	200	0,55	29	9210	45,83	—
	300	0,55	41	9210	30,56	—
	400	0,55	50	9210	22,92	—
	1000	0,55	105	9210	9,17	8360
TCA-12	1000	0,11	214	11 500	1,83	12 100
	1500	0,11	307	11 500	1,22	12 300
	2000	0,11	381	11 500	0,92	12 500
TCA-11	500	0,11	111	13 800	3,67	13 900
	1000	0,11	213	13 800	1,83	14 500
	1500	0,11	318	13 800	1,22	14 700



Viscosity (under shear rate 4 s^{-1}):
TCA-12 — 11 500 mPa·s, TCA-11 — 13 800 mPa·s, TCE-1 — 9210 mPa·s

Fig. 1. The dependence of the tape thickness from shear rate for tapes obtained from suspensions with different viscosity.

Obtained data well corresponding with theoretical models calculated for tape casting [2]. We suggest that in our case after certain limit suspension properties affect a tape thickness stronger than casting conditions. This assertion is also true not only for high values of shear rate but also for very low. Outside of this region, a major role plays a viscosity of the suspension, its rheological nature of the flow, surface tension, adhesion to the surface and height of suspension column in a reservoir [1, 2].

Based on the obtained data we notice that in certain case the film thickness is 10—20% of the height of the blade gap. Such a significant difference between the height of the blade gap and the thickness of the tape exist due to the low pressure values that create the column of the liquid suspension in the reservoir and the type of the casting machine (stationary blade with the reservoir and the moving substrate). The increase of this pressure leads to an increase in the amount of suspension coming out under the blades and consequently to increase the thickness of the raw tape. At high-pressure values, it is possible to obtain films with a thickness greater than the height of the blade gap [3].

Summary obtained data we can make a conclusion that casting conditions affects tape thickness greatly in diapason of shear rate from 2 to 20 s^{-1} for suspension with a viscosity in the range from 8000 to 15 000 mPa·s. Outside of this shear rate diapason, the main role in tape thickness plays suspension properties.

Rheology analysis and flow behavior of created suspensions. It is clear that the suspension with high viscosity allows obtaining of thicker tapes. But knowing the shear rate and the flow curve of the suspension, we can determine the viscosity and shear rate that acting on the suspension when it passing through the blade gap. The nature of the flow can be established at that certain point. This helps to predict a tape behavior during casting.

A flow behavior depends on suspension composition, type and quantity of components, powder size and its specific surface [4—6].

A suspension viscosity curve on fig. 2 shows a pseudoplastic behavior with a minor thixotropy in the region of the shear rate from 2 to 6 s^{-1} and the zone of reopecia in the region of shear rate values (from 0,1 to 0,5 s^{-1}). This complex nature of the flow can be explained by the presence in a system of nano powder of zirconium oxide and micro powder of nickel oxide in a significant content, as well as the presence of two solvents in the system. It should be noted that the pseudoplastic-thixotropic nature of the flow is traditionally considered to be the most suitable for the methods of tape casting and screen printing [7].

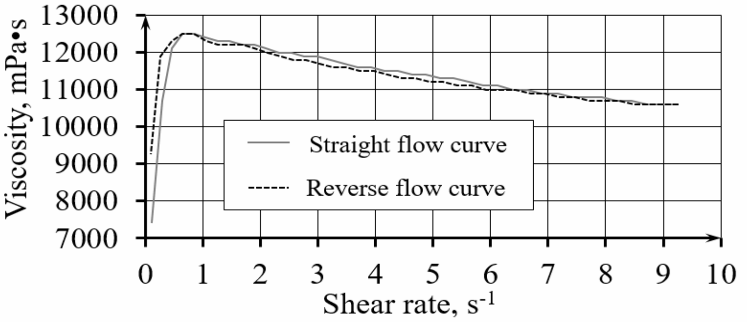


Fig. 2. The dependence of the viscosity from shear rate for TCA-12 suspension.

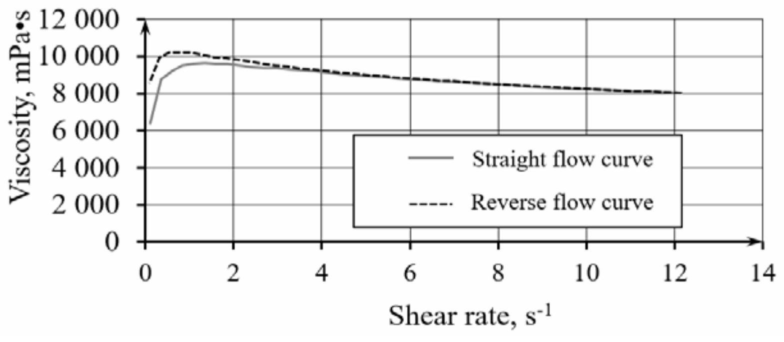
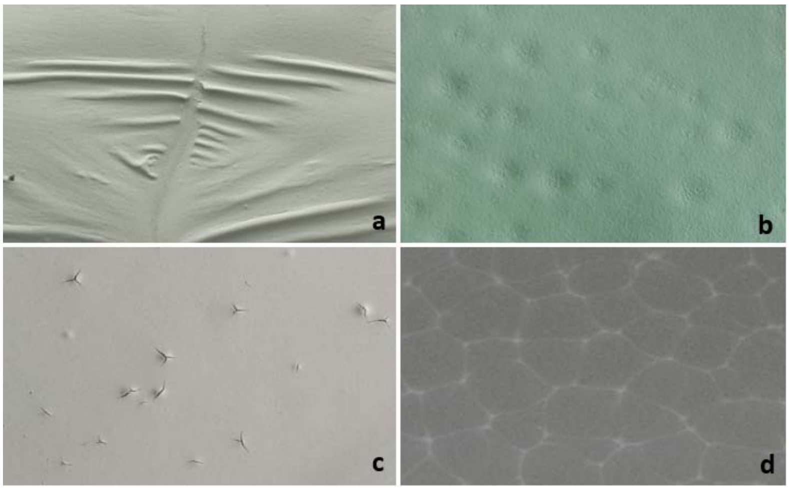


Fig. 3. The dependence of the viscosity from shear rate for TCE-1 suspension.

Unlike the anode, the electrolyte suspension shows rheopexy nature of the flow in a much wider range of shear stress values (from 0.1 to 5 s^{-1}) (fig. 3). In practice, this means that the viscosity of the suspension, after the removal of certain mechanical loads, remains slightly higher than its initial values. This happens due to the structuring of the disperse system during the deformation shift [8]. This phenomenon can be explained by the high content of 8YSZ powder in the TCE-1 suspension. This powder is nanosized and has a high specific surface. In literary sources, it is emphasized that rheopexy will most likely occur in suspensions consisting of anisometric particles. Due to this anisomery, the orientation of the particles can cause solidification that may remain at least for a period of time before reaching its initial liquid state [9]. However, in our case, this suspension behavior has no major effect on the properties of the tape since electrolyte tape have been casted at a high carrier speed and, consequently, at a higher shear stress (9 and 18 s^{-1}). In this region, the suspension exhibits a weak pseudoplastic, almost Newtonian nature of the flow.

Typical defects and methods to avoid them. The anode layer except the electrode function must perform an additional function of a mechanical substrate. For providing this function, it must have a higher thickness to provide a needed mechanical strength. Obtaining of thick tapes is difficult because of formation of defects on the tape surface during drying [10] (fig. 4). To eliminate such defects, the factors that are causing them to appear must be determined.

The analysis of the results indicates that a critical characteristic affects the formation of tape defects is the amount of binder and suspension viscosity. Defects like «central cracking» happen when the amount of binder is not high enough to form a strong polymer matrix that holds powder [7]. The way of solving this issue is to increase binder amount or lower a powder content «Benard cells» forms in thick tapes that cast from low viscous suspensions with a high amount of solid phase due to its thermal motion. To avoid this defect one can reduce the thickness of tape or make a high viscous suspension by reducing solvent, increasing binder amount of using a binder with higher molecular



Defects type:

Fig. 4. Photos of anode tapes surface with most common defects: *a* — “central cracking”; *b* — “hollows”; *c* — “bubbles”; *d* — “Bénard cells”.

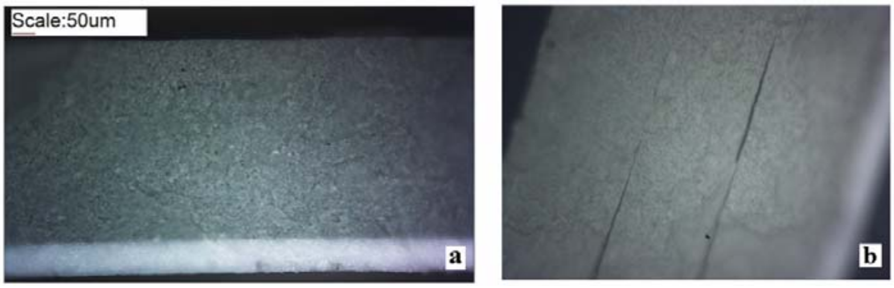


Fig. 5. Cross-section of green half-cell after bending and twisting. Lamination mode: in step-by-step (*a*), one-step (*b*).

weight. The other ways are to keep temperature gradient from bottom to top of the tape as low as it possible. The «bubbles» and «hollows» defect caused by entrapped bubbles of air. This defect can be avoided with a delay before casting when suspension remains some time in doctor blade's reservoir and bubbles of air come on the surface or by using a special deaerating equipment.

Lamination, binder removal and sintering. After obtaining and characterrization tapes were cut to fit the size of a fuel cell and assembled in a multi-layer package consisting of two layers of electrolyte (104 mcm total thickness), 3 layers of the anode (900 mcm total thickness) and one layer of NiO tape with a thickness of 120 mcm. A cross-section of the obtained package shown in fig. 5. The assembled package was heated to 55 °C and pressed in the isostatic laminator. Pressure value was 8000 psi (55 MPa) and dwell time is 20 min.

Practice shows us, that lamination is better to carry out by few steps adding to package by one tape at a time instead of laminating all package in one step. This step-by-step lamination approach allows us to prevent delamination of the green package after bending and twisting (fig. 5) and significant lowering chances of delamination during sintering and in work regime of SOFC.

After lamination obtained package was heated to 450 °C in order to remove binder and plasticizer. Next stage of sintering was conducted at temperature 1400 °C. Then a cathode layer was added to the sintered package by screen printing. Final sintering of SOFC was conducted at temperature 1100 °C.

Conclusions

Suspensions with an optimal composition for each type of SOFC tapes were formulated. The tapes of different thickness and porosity were obtained from different powders. The main factors affecting the properties of the tapes were established. Parameters for casting anode tapes: carrier speed 0.11 m/min, blade gap height 1500 mkm corresponding to the shear rate of 1,222 s^{-1}. Parameters for casting tapes of electrolyte and functional NiO layer: carrier speed 0,55 m/min, blade gap height 400 microns corresponding to the shear rate of 22,92 s^{-1}.

The range of suspension viscosity from which the most qualitative samples of tapes were obtained lays between 12,000 to 22,000 mPa·s. Further increasing the viscosity of the suspensions will result in thicker and stronger tapes, however, high viscosity creates difficulty in mixing and increases the suspension irretrievable losses. The problem of the insufficient thickness of the film can be solved by using in fuel cells several layers of the anode with a small thickness.

Established and classified basic parameters influencing the thickness of the tapes. The dependence of the thickness of the film from the height of the gap is almost linear. The value of the thickness of the tape varies in the range of 10—20% of the value of the height of the gap between the blade and the carrier due to low-pressure values, which creates a column of liquid suspension in the reservoir and type of machine design. The casting parameters significantly affect the thickness of the film in the range of shear rate from 2 to 20 s^{-1} for a suspension with a viscosity in the range from 8000 to 15 000 mPa·s. Outside this range, the main role on the thickness of the tape plays the viscosity of the suspension, its nature of the flow, surface tension, adhesion to the surface and the height of the column of the liquid suspension in the reservoir.

A new approach to the dependency between casting parameters and tape thickness through shear stress was proposed. Rheology properties and flow behavior of the created suspensions were analyzed and explained. Typical defects were identified and methods to avoid them were suggested. Advantages of step-by-step lamination were demonstrated. The obtained tapes were successfully laminated and sintered into an SOFC.

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Плівкове лиття шарів анода і електроліту для твердооксидних паливних елементів

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Описано технологію отримання анодних та електролітних шарів твердооксидних паливних елементів методом плівкового лиття. Оптимальні склади суспензій та параметри лиття встановлено та пояснено на підставі аналізу характеру кривих течії суспензій та напружень, що вони зазнають під час лиття. Виявлено типові дефекти та запропоновано методи їх уникнення. Показано переваги поетапного ламінування.

Ключові слова*: плівкове лиття, твердооксидні паливні елементи, анод, електроліт, суспензії, реологія, дефекти плівок.*

Плёночное литьё слоёв анода и электролита для твердооксидных топливных элементов

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Описана технология получения анодных и электролитных слоев твердооксидных топливных элементов методом пленочного литья. Оптимальные составы суспензий и параметры литья установлены и объяснены на основании анализа характера кривых течения суспензий и напряжений, которые они испытывают во время литья. Обнаружены типичные дефекты и предложены методы их предотвращения. Показаны преимущества поэтапного ламинирования.

Ключевые слова: *плёночное литьё, твердооксидные топливные элементы, анод, электролит, суспензии, реология, дефекты пленок.*