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Study of slurry spin coating technique parameters for the fabrication of anode-supported YSZ Films for SOFCs

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Abstract

A slurry spin coating method was developed to fabricate gas-tight anode-supported YSZ films for solid oxide fuel cells (SOFCs). Several technique parameters for slurry spin coating, such as the slurry viscosity, spinning speed, number of coating cycles, film thickness and their effects on YSZ electrolyte film were investigated. SEM results, open-circuit voltage (OCV) values and cell performance indicated that these parameters had crucial and obvious influences on YSZ film quality and fuel cell performance. Based on the optimized parameters, anode-supported YSZ films and several single fuel cells were successfully fabricated and tested. An OCV as high as 1.06 V was obtained at 800 °C and maximum power densities of 900, 1567, 2005 mW cm^{-2} were achieved at 700, 750, 800 °C, respectively, using hydrogen as fuel and ambient air as oxidant.

Keywords: Solid oxide fuel cells; YSZ electrolyte film; Slurry spin coating; Technique parameters

1. Introduction

The solid oxide fuel cell (SOFC) has many merits, such as low environmental pollution, use of a variety of fuels, high conversion efficiency and is a promising power generation technology for the future [1,2]. The conventional operating temperature is 800–1000 °C, which is high and causes many material and technology issues. In order to reduce the operating temperature down to 600–800 °C, anode-supported SOFCs with thin electrolyte films were developed, with several benefits, such as cost reduction and long life [3,4]. Slurry coating [5–7], spin coating [8,9], tape casting [10], spray coating [11], CVD [12], screen-printing [13] are several methods used in fabricating thin YSZ electrolyte films with high quality. However, most cell fabrication techniques need complex drying, baking or sintering process.

Slurry spin coating is a new method developed in our laboratory recently [14]. It is a good combination of slurry coating and spin coating; the slurry is prepared by mixing electrolyte powders with binders consisting of ethyl cellulose and terpineol. The fabrication process requires no strict baking and cooling rates of 5–20 °C min^{-1} and only a few coating cycles are needed. YSZ, NiO-YSZ and $Ce_{0.8}Sm_{0.2}O_{1.9}$ impregnated $La_{0.7}Sr_{0.3}MnO_3$ (LSM) were used as the electrolyte, anode and cathode material, respectively. A maximum power density of 0.42 W cm^{-2} was achieved at 650 °C in previous work [15]. Air and dry hydrogen were used as oxidant and fuel, respectively. Although such an excellent result has been achieved in the basic investigation, it still needs systematic studies to optimize the parameters of the slurry spin coating method since which are important for the quality of electrolyte film and repeatability of the fabrication process. The important parameters for slurry spin coating include slurry viscosity determined by slurry composition, spinning speed, number of coating cycles and electrolyte film thickness.

In this paper, the roles of these important parameters are analyzed and the effects of them on YSZ films studied in detail. The slurry spin coating technique was optimized to fabricate perfect anode-supported YSZ films with excellent fuel cell performances.

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Table 1
Slurry composition (e.g. slurry 30Y2E means YSZ content of this slurry is 30 wt.% and ethyl cellulose content is 2 wt.%)

Slurry category number	30Y2E	30Y4E	30Y6E	20Y5.5E	30Y5.5E	40Y5.5E
YSZ content in slurry (wt.%)	30	30	30	20	30	40
Ethyl cellulose content in binder (wt.%)	2	4	6	5.5	5.5	5.5

2. Experimental

2.1. Slurry preparation

The slurries were prepared by mixing YSZ powder (TZ-8Y, Tosoh Corporation, Tokyo, Japan) with a homemade organic binder consist of ethyl cellulose (analytical reagent, A.R., Dongfeng Chemical Reagents Plant, Wenzhou, China) and terpineol (A.R., Tianjin Kermel Chemical Reagents Development Centre, Tianjin, China). They were divided into six categories by their different composition, which is shown in Table 1. In the first three categories, the YSZ content was fixed, while the ethyl cellulose content varied. In the latter three, the ethyl cellulose content was fixed, while the YSZ content was varied. In all six categories, the materials were mixed together and ground in an agate mortar for 2 h to obtain a homogeneous and stable slurry.

2.2. Slurry viscosity measurement

The apparent slurry viscosities were measured by a NDJ-99 rotation viscometer (Chengdu instrument plant, Chengdu, China) at room temperature (∼22 °C).

2.3. Anode substrate preparation

NiO was synthesized by the glycine-nitrate process (GNP) [14], and the resultant foaming ash was calcined in air at 600 °C for 2 h to get a pure NiO powder. NiO, YSZ and a flour pore former were mixed in an agate mortar and ground for 3 h in the weight ratio of 5:5:1.7. The mixture was uniaxially pressed into pellets of 13 mm in diameter, and then precalcined at 1000 °C for 2 h in air to ensure adequate strength for anode substrates.

2.4. Fabrication YSZ film by slurry spin coating

A typical slurry spin coating process (except for final sintering) included three steps: (1) an adequate amount of slurry was dripped onto the anode substrate which was supported by a spinner (KW-4A type, Microelectronics Center of Chinese Academy); (2) after setting the spinning speed and time (120 s), the spinner was started; (3) the film with substrate was heated up with an average heating rate of ∼17 °C min^{-1} to 420 °C and baked for 10 min at 420 °C, thus a full slurry spin coating cycle was finished. In order to get a film with a suitable thickness, multiple coating cycles were needed. And finally, the baked film and substrate were co-sintered at 1400 °C for 4 h. The technique parameters, such as slurry composition, spinning speed of rotation and the number of the coating cycles were varied in this experiment. Using different process parameters, 15 different film samples with the same anode substrates were fabricated and the detailed processing conditions are listed in Table 2. They are divided into three groups by different spinning speed and coating cycles, and in one group the slurry compositions were different. So each sample has a unique list of process parameters. Group 1 were the first six samples with the same spinning speed of 6 krpm and one coating cycle, group 2 contains the followed three with the same spinning speed of 10 krpm and one coating cycle, group 3 were the last six with the same spinning speed of 6 krpm and three coating cycles.

2.5. Cathode preparation

$La_{0.7}Sr_{0.3}MnO_3$ (LSM, prepared by sol–gel method) and activated carbon (A.R.) mixture was deposited on the electrolyte film and then sintered at 1100 °C for 4 h. The sintered cathodes were impregnated by the $Sm_{0.2}Ce_{0.8}$ $(NO_3)_x$ saturated solution [16], and calcined at 850 °C for 1 h.

2.6. Cell test and YSZ film microstructure

Silver paste (DAD-87, Shanghai Research Institute of Synthetic Resin, China) was used to seal the fuel cell onto an alumina tube. Each cell was tested with four-probe method in a furnace at temperatures from 700 to 800 °C. Dry hydrogen was used as the fuel, and ambient air as the oxidant. The cell performance and electrochemical impedance spectra were measured by an electrochemical interface Solartron SI 1287 in combination with an impedance analyzer SI 1260. The impedance spectra were collected in the frequency range from 91 kHz to 0.1 Hz.

The microstructure of the cells after the electrochemical test was characterized by a JEOL JSM6480LV scanning electron microscope.

3. Results and discussion

3.1. Factors of slurry spin coating

Slurry viscosity, spinning speed of rotation and number of coating cycles are important to the YSZ film thickness. During the slurry spin coating process, the slurry must be flowed and spread along the radial direction. The spreading velocity is determined by both the spinning speed and the slurry viscosity. A higher slurry viscosity or lower spinning speed will cause a smaller spreading velocity.

On the other hand, by observing the progress of this experiment, it has been found that during the process of slurry spin coating, terpineol evaporated and YSZ/ethyl cellulose concentrations rose quickly as a result of the terpineol evaporation, then the film became ‘frozen-in’ with the non-volatile material contents rising and the film thickness fixed. This phenomenon was

Table 2
Parameters of different samples (e.g. sample 30Y2E6-1 means YSZ content of the source slurry is 30 wt.%, ethyl cellulose content of the source slurry is 2 wt.%, spinning speed of rotation is 6 krpm and coating cycle is 1 in fabrication)

	Group number							
	Group 1	Group 1	Group 1	Group 1	Group 1	Group 1	Group 2	Group 2
Sample name	30Y 2E6-1	30Y 4E6-1	30Y 6E6-1	20Y5.5E6-1	30Y5.5E6-1	40Y5.5E6-1	20Y5.5E10-1	30Y5.5E10-1
Slurry category number	30Y2E	30Y4E	30Y6E	20Y5.5E	30Y5.5E	40Y5.5E	20Y5.5E	30Y5.5E
Spinning speed (krpm)	6	6	6	6	6	6	10	10
Coating cycles	1	1	1	1	1	1	1	1

	Group number						
	Group 2	Group 3	Group 3	Group 3	Group 3	Group 3	Group 3
Sample name	40Y5.5E10-1	30Y2E6-3	30Y4E6-3	30Y6E6-3	20Y5.5E6-3	30Y5.5E6-3	40Y5.5E6-3
Slurry category number	40Y5.5E	30Y2E	30Y 4E	30Y6E	20Y5.5E	30Y5.5E	40Y5.5E
Spinning speed (krpm)	10	6	6	6	6	6	6
Coating cycles	1	3	3	3	3	3	3

similar to Bornside et al.'s report [17], though they used totally different slurries in another field. Furthermore, because the terpineol was a major part of the slurry by weight, it is believed that though different slurries have different YSZ or ethyl cellulose contents, the time from the starting stage to the 'frozen-in' stage was the same. So in the same spinning time, the film thickness is determined by both viscosity and spinning speed [17–19]. The higher the slurry viscosity or the lower the spinning speed, the thicker the YSZ film.

Moreover, it is obviously that more coating cycles can result in a larger film thickness. And defects in the underlying layer can be repaired by the upper ones. So the number of coating cycles is another parameter for investigation.

By the analysis above, slurry viscosity, spinning speed of rotation, coating cycles were selected as the dominant process parameters for slurry spin coating and were investigated carefully. In this study, they were considered as three initial parameters and they have direct effects on film thickness. Film thickness was considered as an intermediate parameter. It has effects on open-circuit voltage (OCV), ohmic resistance, microstructure and power density of SOFC. These four parameters were considered as the ultimate parameters, which characterise the performance of fuel cells. So the initial parameters have indirect and important effects on the final SOFC performance. Shown in Fig. 1 is the logical relationship among these parameters. By optimizing the process parameters, high quality electrolyte films can be fabricated with good repeatability using slurry spin coating technique.

Spin coating is a widely used technique. When it is used in semiconductor or microelectronic manufacturing process, it is important that the film has a flat surface. And much work has done to reach this aim [17–21]. But in the fabrication of a SOFC, a dense electrolyte film with a suitable thickness is required.

3.2. Effects of initial parameters on the film thickness

3.2.1. Effects of viscosity on the film thickness

Viscosities of slurries with different YSZ/ethyl cellulose concentrations were measured, and the values are shown in Table 3. There exists a big difference between the viscosity values. And qualitatively, the higher YSZ or ethyl cellulose contents the lower the slurry viscosities. So, adjusting either the YSZ or ethyl cellulose content can influence the slurry viscosity.

The thickness of the final films (films sintered at high temperature) of group 1 was obtained by analyzing the cross-section SEM images. The results are listed in Table 3. Samples 30Y4E6-1 and 20Y5.5E6-1's source slurries have similarly low viscosities (29.8 and 35.7 Pa s, respectively), and so a similar thickness of the "green" films (films which have not been sintered at high temperature) would be expected. However, sample 20Y5.5E6-1 was thinner than sample 30Y4E6-1 obviously. The thickness values of samples 30Y4E6-1 and 20Y5.5E6-1 were 3.3 and 2.1 μm, respectively. This was because the source slurry of sample 20Y5.5E6-1 had a lower YSZ content than the source slurry of sample 30Y4E6-1 and after baking and sintering, only the YSZ was left to form the final films. In other hand, for samples 30Y4E6-1 and 20Y5.5E6-1, the ratio of the final YSZ film thickness was close to the ratio of the YSZ contents of the slurries. So, it can be presumed that the green films of these two samples have a similar thickness. The films of samples 30Y6E6-1 and 30Y5.5E6-1 were thicker and had similar higherin viscosities.

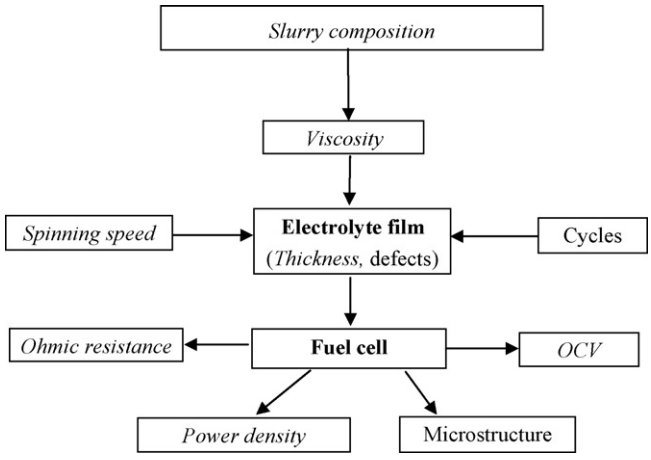

Fig. 1. Logic diagram for the relationship of the parameters.

Table 3
Final film thickness of samples in group 1

	Sample name				
	30Y4E6-1	30Y6E6-1	20Y5.5E6-1	30Y5.5E6-1	40Y5.5E6-1
Apparent viscosity (Pa s)	29.8	107	35.7	65.1	384
Film thickness (μm)	3.3	7.8	2.1	7.3	12.1

Table 4
Coating cycles effect on film thickness (6krpm)

Source slurry category number	30Y4E	30Y6E	20Y5.5E	30Y5.5E	40Y5.5E
Film thickness (μm)					
One cycle t_1 (group 1)	3.3	7.8	2.1	7.3	12.1
Three cycles t_3 (group 3)	10.5	22.8	7.5	19.1	35.4
t_3/t_1	3.2	2.9	3.6	2.6	2.9

Sample 40Y5.5E6-1 had the thickest film and the YSZ content of its source slurry were also the highest. So from a qualitative viewpoint, both higher viscosity and higher YSZ content caused a thicker final YSZ film.

3.2.2. Effects of spinning speed on film thickness

Electrolyte film thickness data of groups 1 and 2 were obtained and are shown in Fig. 2. Generally, the films in group 2 were thinner than the corresponding films in group 1, and this phenomenon was caused by a higher spinning speed. Emslie et al. [19] obtained the equation:

$$h(t) = h_0 \left(\frac{1 + 4\rho\omega^2 h_0^2 t}{3\eta} \right)^{-1/2} \quad (1)$$

$h(t)$ is the film thickness, h_0 a constant, ρ the density of the slurry, ω the angular velocity and η is the viscosity of the slurry. In this research, the value of $4\rho\omega^2 h_0^2 t/3\eta$ was far more than 1. So, Eq. (1) can be simplified as

$$h(t) = \frac{h_1}{\omega} \quad (2)$$

h_1 is a constant different to h_0. By Eq. (2), thickness ratio of YSZ films fabricated at 10 and 6 krpm was 0.6. And from the data in Fig. 2, thickness ratios of YSZ films fabricated at 10 and 6 krpm from slurry 20Y5.5E, 30Y5.5E and 40Y5.5E, respectively, were 0.67, 0.71 and 0.67. They were close to the theoretical value. So it theoretically proved that in the slurry spin coating technique, the spinning speed does have an important and obvious effect on film thickness. The relationship between the spinning speed and film thickness somewhat satisfies Emslie et al.'s equation.

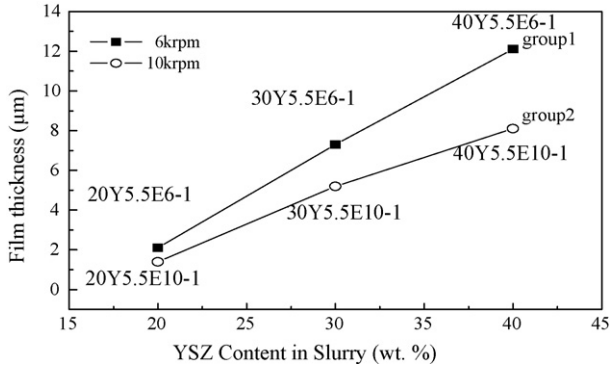

Fig. 2. Spinning speed effects on film thickness.

3.2.3. Effects of coating cycles on film thickness

Table 4 shows the thickness data obtained by different coating cycles. Comparing the data of groups 1 and 3, the thickness of group 3 was about three times of thickness of group 1. So a linear relationship between the film thickness and the coating cycles can be found evidently. Adjusting the coating cycles can control film thickness.

3.3. Effects of film thickness on cell performance

3.3.1. Effects of film thickness on the microstructure of electrolyte film

Typical SEM images of the surface and cross-section of YSZ electrolyte films are shown in Fig. 3. Few pores or cracks are observed in the electrolyte film regions of Fig. 3a and b, and the film adhered well to the porous anode substrate. The film thickness of sample 40Y5.5E6-1 was 12.1 μm. In Fig. 3c and d, the film thickness of sample 30Y4E6-1 was 3.3 μm and it seems too thin to be sintered dense enough. There exist lots of pores and micro-cracks on the surface of the film.

From the observation of SEM images of all 15 samples, we found that in the slurry spin coating technique when the thickness of an YSZ film was larger than ~8 μm, the film surface seems dense. On the contrary, if an YSZ film was similar or thinner than ~5 μm, there would exist some pores or micro-cracks on the film surface. So in this technique, film thickness has an obvious and direct effect on the microstructure of the YSZ film.

3.3.2. Effects of film thickness on the OCV of SOFC

The OCV data of 15 samples with different film thickness were obtained and are plotted in Fig. 4. As shown, in the range of 2–10 μm, the thicker film has the higher OCV. This indicated

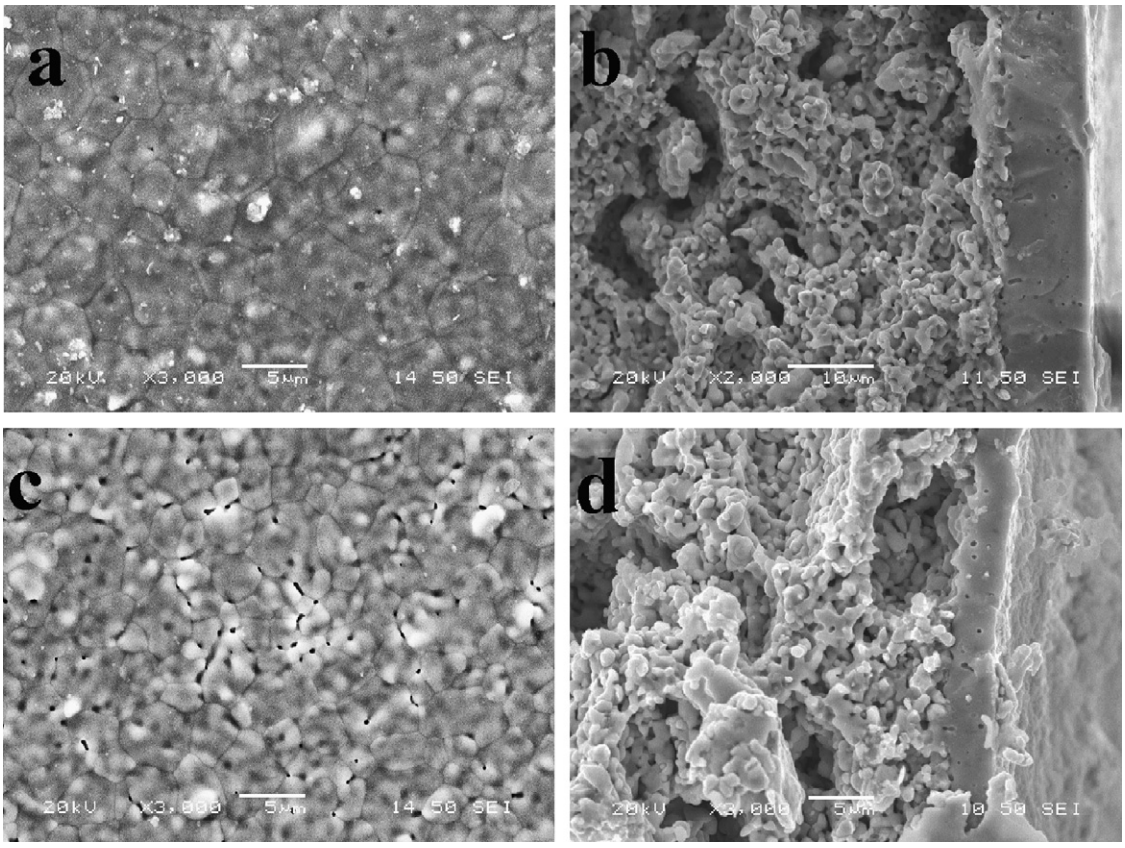

Fig. 3. SEM images of the electrolyte films: (a) surface, sample 40Y5.5E6-1. (b) Cross-section, sample 40Y5.5E6-1. (c) Surface, sample 30Y4E6-1. (d) Cross-section, sample 30Y4E6-1.

that there existed gas leakage in the samples with a 2–10 μm film thickness. Low OCVs were caused by gas leakage, and the YSZ films were too thin to resist gas leakage. One can decrease the pores or pinholes in YSZ film, diminish the gas leakage and in turn increase the OCV by utilizing a thicker slurry or more coating cycles to enhance the film thickness. In the range of 12–36 μm, high OCV close to the theoretical value was obtained in every sample. This indicated that there existed few pores or cracks or pinholes in YSZ films and the films were dense enough to effectively resist gas leakage. So in this range of thickness, the film thickness has no obvious relationship with the OCV of the fuel cell.

3.3.3. *Effects of film thickness on ohmic resistance*

Specific resistances (Ohmic ASR) of theYSZ films with different thickness were obtained from impedance spectra; the results are plotted in Fig. 5. As shown, the thicker the film the higher the resistance and an approximate linear relationship between the Ohmic ASR and thickness can be found. So, when the YSZ film was dense and a high OCV was obtained, the thinner film SOFC had a better performance. Combining the values of OCVs in Fig. 4 and the Ohmic ASRs in Fig. 5, it seems that a ∼10-μm electrolyte film is the best choice for getting high quality electrolyte films which can match the requirements of both low Ohmic ASR and high OCV.

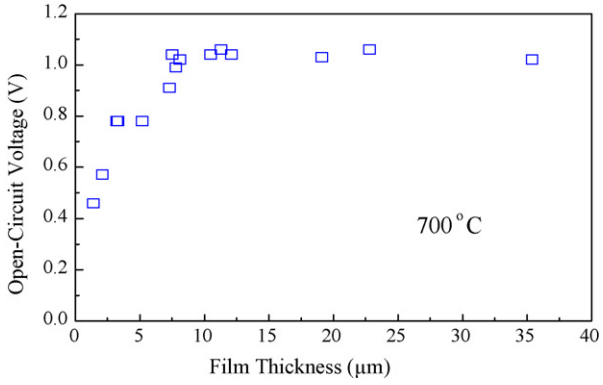

Fig. 4. Effects of film thickness on OCV of SOFC.

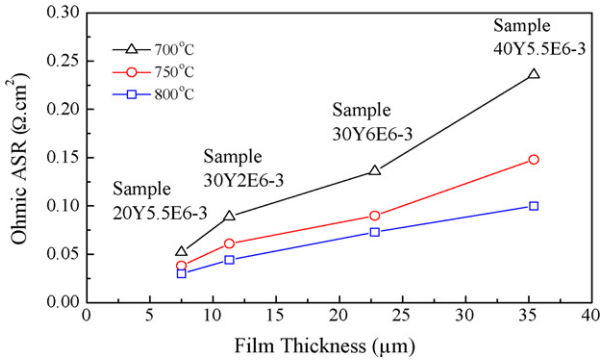

Fig. 5. Effects of film thickness on ohmic resistance of the cells (group 3).

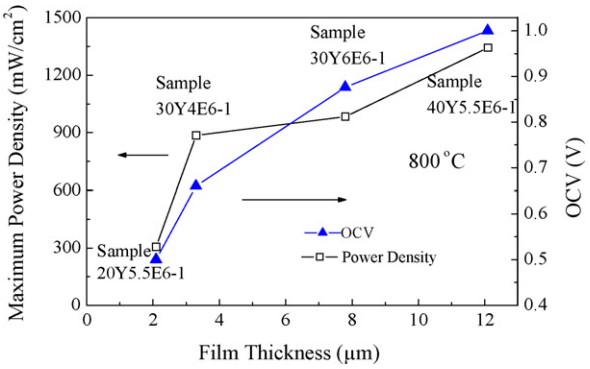

Fig. 6. Comparison of fuel cell performances at 800 °C (group 1).

3.3.4. *Effects of film thickness on power density*

Fig. 6 shows the output performance of samples 20Y5.5E6-1, 30Y4E6-1, 30Y6E6-1 and 40Y5.5E6-1 at 800 °C. The four samples were fabricated with one coating cycle and have a small film thickness. As shown, in a certain range of thickness, the thicker the film the better the performance. In this range, although the Ohmic ASRs were low, the cell performances were not good. The single layer YSZ films were too thin to resist gas leakage. Gas leakage diminished the OCV and the power density of the fuel cell.

Fig. 7 plots the maximum power densities of samples 20Y5.5E6-3, 30Y2E6-3, 30Y6E6-3 and 40Y5.5E6-3 at 700–800 °C. The four samples were fabricated with three coating cycles and have a relative larger film thickness. Comparing the performances of group 1 in Fig. 6 and group 3 in Fig. 7, it can be seen that the films fabricated with three coating cycles have a much better average quality than the films fabricated with a single coating cycle. So in order to obtain a high performance fuel cell, an appropriate film thickness that can effectively resist gas leakage is necessary. The process of fabrication had several coating cycles with an intermediate spinning speed of rotation to adjust the film thickness. Three coating cycles was the most simple and practical condition.

In another aspect, as shown in Fig. 7, all four samples provide excellent performance at intermediate temperatures lower than 800 °C. This indicates that via a slurry spin coating, the electrolyte films can always be successfully fabricated using different slurries with a wide range of YSZ or ethyl cellulose

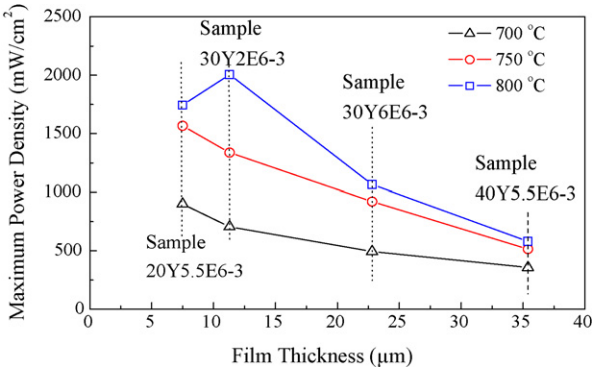

Fig. 7. Comparison of fuel cell performances ranging from 700 to 800 °C (group 3).

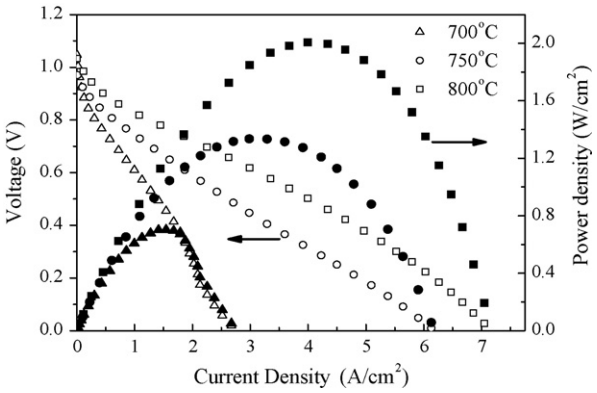

Fig. 8. Voltage and power density for the cell of sample 30Y2E6-3.

contents. That is the reason why good YSZ films could be fabricated using arbitrary slurries without optimization in our previous work [15]. Moreover, among the four samples, roughly the thinner film had the better performance. The quality of films from relative low viscosity slurries was better than from relatively high viscosity slurries. This is because all these fuel cells have high OCVs, and YSZ films from high viscosity slurries have a large thickness that generated high ASRs. Therefore, in the slurry spin coating technique, the electrolyte film with the highest quality comes from a relative low viscosity slurry. The process of fabrication requires three coating cycles and the thickness of that film is about 10 μm.

As shown in Fig. 8, the maximum power densities of sample 30Y2E6-3 were 704, 1337, 2005 mW cm^{-2} at 700, 750, 800 °C, respectively, using hydrogen as fuel and ambient air as the oxidant. In different samples of group 3, a maximum power density of 900, 1567, 2005 mW cm^{-2} were achieved at 700, 750, 800 °C, respectively. This performance proved that high quality electrolyte films could be successfully fabricated via slurry spin coating using optimized parameters.

4. Conclusion

In this paper, several important process parameters for slurry spin coating and their effects on the produced YSZ electrolyte films were investigated. These parameters were: slurry viscosity, spinning speed, coating cycles and film thickness. The process of fabrication of the YSZ film has been optimized. Using a slurry spin coating technique, the electrolyte film with the highest quality is obtained from a relative low viscosity slurry and the process of fabrication requires several coating cycles with an intermediate spinning speed to adjust the film thickness to ~10 μm. Three coating cycles was the most simple and practical condition. With optimized parameters, an OCV as high as 1.06 V was obtained, and a maximum power density of 900, 1567, 2005 mW cm^{-2} was achieved at 700, 750, 800 °C, respectively.

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