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A facile and environment-friendly method to fabricate thin electrolyte films for solid oxide fuel cells

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ABSTRACT

A facile and environment-friendly method, the so-called vertical deposition (abbreviated as VD) method, is used to prepare thin yttria-stabilized zirconia (YSZ) films ($\leq$5 μm) for solid oxide fuel cells (SOFCs). The YSZ films are self-assembled by VD process based on capillary force. The influence of experimental conditions (e.g. concentration of YSZ dispersion, deposition times, and sintering procedure) on the morphology of the films produced and thereby on the performance of SOFC devices is investigated. The single cell utilizing a 5 μm dense YSZ film as solid electrolyte achieves a high open circuit voltage of 1.05 V which remains stable at 700 °C for 4 h. The peak power density is 0.4 W cm^{-2} at 800 °C for the phase inversion anode-supported fuel cell composed of an YSZ electrolyte film of 5 μm thick. The VD method developed herein is promising for preparing ultra-thin electrolyte films for SOFCs.

1. Introduction

Recently, great interests arose for the combined heat and power generation system based on solid oxide fuel cells (SOFCs). Traditional SOFCs operate at relatively high temperature (800–1000 °C), resulting in long start-up time as well as mechanical and chemical compatibility issues. Lowering the operation temperature down to 600–800 °C can reduce the cost of the interconnection materials and avoid the degradation problems resulted from thermal cycling or diffusion at interfaces [1–4].

The electrolyte film is one of the most important components of SOFC device and it must be impermeable to both oxidant and fuel gases at both room and operation temperatures. Among the many ceramic electrolyte materials, yttria-stabilized zirconia (YSZ) is the most common choice because of its high ionic conductivity and good stability at 800–1000 °C [5]. However, as the operation temperature decreases, the ionic conductivity of YSZ and thereby the fuel cell power output decrease. At present, there are mainly two strategies to solve this problem, including replacing YSZ with other materials having higher ionic conductivity than YSZ (such as samaria- or gadolinia-doped ceria [6–10]) and reducing the thickness of the electrolyte films [11,12].

There has been considerable flexibility in the fabrication of YSZ films, and tape-casting [13], dip-coating [14], plasma spraying [15], sol–gel [16], and screen printing [17] routes have been described. Generally, the thickness of the electrolyte films produced by these methods is in the range of 10–50 μm. Ding et al. [18] investigated the influence of the thickness of $Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC) electrolyte membranes on the electrical performance of the anode-supported SOFCs. Fuel cells consisting of dense GDC electrolyte membranes of 1–75 μm thick have been prepared. The results showed that reducing the thickness of the GDC electrolyte membrane can improve the electrical performance of the anode-supported SOFCs and a single cell with a 5 μm thick GDC electrolyte membrane demonstrated the highest maximum power density. Hashida et al. [19] prepared an anode-supported fuel cell consisting of a 3 μm thick GDC electrolyte membrane. The maximum power density was 0.99 W cm^{-2} at 600 °C which is very promising performance for intermediate temperature SOFCs. Thus, it is indicated that reducing the thickness of the electrolyte membrane is favorable for improving the performance of SOFCs.

A variety of thin film deposition methods have demonstrated the feasibility of synthesizing YSZ films ranging from 500 nm to 2 μm, including chemical vapor deposition (CVD) [20], pulsed laser deposition (PLD) [21], and atomic layer deposition (ALD) [22], etc. However, problems exist for each method. For example, CVD method requires a high reaction temperature and produces corrosive gases during the deposition process [20]. The thin films

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deposited using PLD method often contain large particles of the sputtering target due to the difficulty of melt in the deposition process. ALD method requires expensive equipment and strict control of the experimental conditions [23]. For all these methods, they have relatively low deposition rate.

Since the above mentioned deposition methods are not suitable for practical application, efforts should be made to check out the reason why the dense YSZ films prepared using the conventional methods are so thick. Generally, for these methods, YSZ powders are dispersed in organic solvents and a great quantity of organic additives acting as binder, dispersant and plasticizer are added to form the precursor slurry. Then, after tape-casting or other molding process, the tapes are formed. After drying, a large amount of micron-scale holes are left in the tapes because of the evaporation of organic reagents. Thus, in order to get dense films, a high temperature sintering at 1400–1500 °C must be performed. However, even after sintering, small amount of nano-scale holes still exist and gas leakage easily takes place if the film is very thin. As the thickness of the electrolyte film increases, the holes are nonpenetrating and gas permeation is prevented.

In contrast to the burgeoning literature on the synthesis of YSZ thick films, studies on the solution to this dilemma between ultra-thin and thick YSZ films are relatively sparse. For preparing colloidal crystals, vertical deposition (abbreviated as VD) method introduced by Colvin et al. [24] has gained considerable attentions [25,26]. Monodisperse colloidal sphere dispersions are left to evaporate naturally to deposit high-quality thin films on a vertically held substrate by the meniscus of an evaporating solvent. VD method is carried out based on capillary force and the colloidal crystals produced are cubic close-packing. Therefore, if we apply VD method to produce ceramic electrolyte tapes, the densely packed structure will facilitate the densification of the tapes. In this study, we proposed the application of VD method to prepare dense YSZ electrolyte films within several microns thick. The influence of deposition parameters, i.e., concentration of YSZ dispersion, deposition times, and sintering procedure on the morphology of the films has been investigated.

2. Experimental

Preparation of NiO/YSZ anode substrates. Porous NiO/YSZ anode substrates were prepared using phase inversion method [27,28]. Commercial NiO (Inco, USA) and YSZ (TZ-8Y, Tosoh, Japan) powders were used as received and other reagents were all analytical grade. Raw materials in a proportion of 31.9 wt% NiO, 25 wt% YSZ, 35.5 wt% N-methyl-2-pyrrolidone (solvent), 7.1 wt% polyethersulfone (binder), and 0.5 wt% polyvinylpyrrolidone (dispersant) were mixed and ball milled for 24 h to form the viscous slurry. The slurry was degassed by a vacuum-assisted apparatus for 30 min, and then poured into Φ 16 mm, 2 mm thick round molds. Subsequently, the molds were immersed in a water bath at room temperature for more than 24 h to solidify the NiO/YSZ layer, and green NiO/YSZ pellets were then formed. The green pellets were heated at 600 °C for 2 h to remove the organic polymers, followed by sintering at 1200 °C in ambient non-flowing air atmosphere for 2 h. The obtained anode supports were Φ 13 mm and 1 mm thick.

Preparation of YSZ films. For the deposition of YSZ films on porous NiO/YSZ anode supports, a typical YSZ dispersion was prepared according to the following steps. 2.5 wt% YSZ powders were ultrasonically dispersed in 96.1 wt% de-ionized water for 30 min. Then, 0.2 wt% sodium hexametaphosphate and 1.2 wt% polyvinyl alcohol acting as dispersant and binder, respectively, were added and mechanically stirred for 1 h.

Before use, the anode supports were ultrasonically cleaned in ethanol and acetone for 10 min, respectively. Then, an anode support was vertically immersed into 15 mL YSZ dispersion in a 25 mL glass beaker. The beaker was placed on a vibration-free bench in a temperature-controlled drying oven to keep out external airflow and contamination. The oven was set at 70 °C until the solvent was completely evaporated. The schematic diagram of the principle of VD process is shown in Fig. 1. During the solvent evaporation process, YSZ particles self-assembled into densely packed films with the help of capillary force. YSZ films with different thickness could be obtained by changing the deposition parameters. The YSZ films produced were co-sintered with the anode supports in air at 1300 °C for 20 h [14].

Characterization. Surface and cross-section views of the samples were observed by scanning electron microscopy (SEM, FEI Quanta200f, Netherland). Fractured cross-sections were prepared manually. Laser particle-size analyzer (OMEC, LS900) was used to evaluate the YSZ particle size distribution. For characterization of the electrochemical performance of the single fuel cell, commercial $La_{0.8}Sr_{0.2}MnO_3$ (LSM)/YSZ and LSM powders (Nextech, USA) were screen-printed on the YSZ electrolyte one after the other to form the cathode functional and current collecting layers. The cathode was sintered at 1100 °C for 2 h. The single cell was tested with two-probe method in a tubular furnace [29]. For all the tests, humidified hydrogen with a flow rate of 100 sccm was used as the fuel and ambient air as the oxidant. The cell performance was measured by Arbin fuel cell testing equipment (USA).

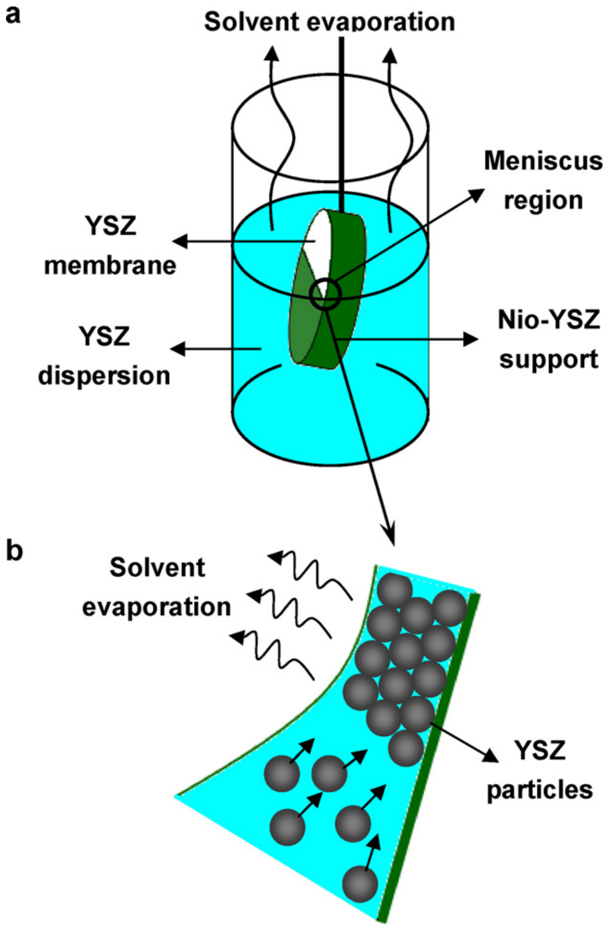

Fig. 1. Schematic diagrams of (a) the equipment required for VD process and (b) the working principle of VD method.

3. Results and discussion

3.1. Characterization of film morphology

The schematic diagram of the self-assembly principle of VD process is shown in Fig. 1. When YSZ particles are dispersed in a thin layer of liquid, lateral capillary force causes an attractive interaction between them. Particles are pushed together and nucleate, forming a densely packed monolayer. Then, flow of solvent brings in more particles and the monolayer grows. Thus, the force of surface tension in the meniscus region is responsible for bringing near the particles, consolidating them into a crystal. The efficiency of the vertical deposition relies on the balance between solvent evaporation and particle sedimentation. When sedimentation is faster than solvent evaporation, the self-organization of the particles does not take place. Conceptually similar to the Langmuir–Blodgett methods for film deposition, VD method principally can create films on nearly any vertical surface, which relies on capillary force to organize the particles.

It is well known that the synthesis of monodisperse colloidal spheres is one of the most important preconditions for preparing

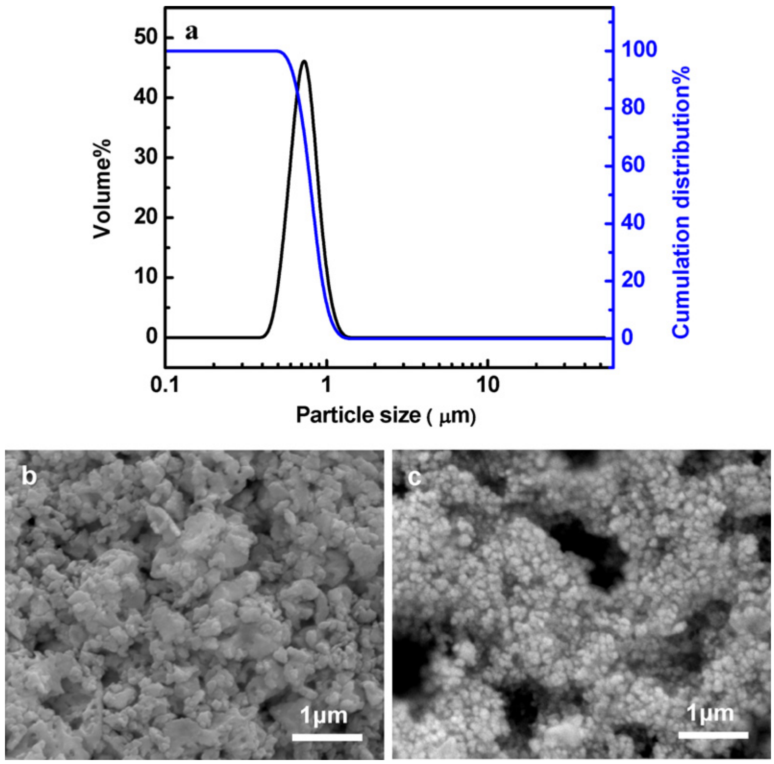

Fig. 2. (a) Particle-size distribution curve of the commercial YSZ powder dispersed in de-ionized water; SEM micrographs of (b) the YSZ film prepared by VD process before sintering and (c) the tape-casting green tape before sintering.

colloidal crystals, since polydisperse spheres will destroy the long-range ordering [25]. Fig. 2a shows the particle-size distribution curve of the commercial YSZ powder dispersed in de-ionized water. It is indicated that the D50 value of the cumulative distribution curve is 0.64 μm and the YSZ particles are nearly monodisperse, since there is only one peak in the differential distribution curve. The SEM micrograph of the YSZ film prepared by VD method before sintering is shown in Fig. 2b. Obviously, one can see a compact film without micron scale holes is deposited. As a comparison, Fig. 2c shows the SEM micrograph of the YSZ film prepared by tape-casting method. Generally, a great deal of organic reagents is added to the tape-casting slurry. Due to the evaporation of organic reagents, many micron scale holes are left in the tapes, as shown in Fig. 2c. Thus, in order to get dense YSZ films, a high temperature sintering at 1400–1500 °C has to be performed onto these films prepared by tape-casting method. The compact films prepared by VD method contain trace amount of micron scale holes and a dense YSZ film could be obtained by sintering at relatively low sintering temperature, which is an advantage of this method. After preliminary study, 1300 °C is found to be sufficient for the densification of YSZ films.

Further investigations indicate that the morphology of the YSZ films is influenced by the experimental conditions, including the concentration of YSZ dispersion and the deposition times. Fig. 3a and b shows the surface and cross-section SEM micrographs of the YSZ film prepared by repeating VD process ten times using 1 wt% YSZ dispersion. Obviously, holes and cracks are easily seen. As shown in Fig. 2b, the average particle size of YSZ is 0.64 μm, whereas the thickness of the YSZ film is only 1.8 μm after ten times of deposition. Thus, it is indicated that each layer of YSZ film after each time of deposition is not a continuous compact film because of the low concentration of YSZ dispersion. Consequently, during the sintering process, the shrinkage of the YSZ film results in the formation of holes and cracks. Therefore, too low concentration is not favorable for producing uniform and dense YSZ films. Fig. 3c and d shows the cross-section SEM micrographs of YSZ films prepared by repeating VD process five times using 1.5 wt% and 2.0 wt% YSZ dispersion, respectively. The thickness of the YSZ films is 2.8 and 3.5 μm, respectively. As expected, as the concentration of YSZ dispersion increases, more YSZ particles self-assemble into more continuous and thicker films. However, sedimentation of YSZ particles occurs when the concentration of YSZ dispersion further increases to 3.0 wt% (at the deposition temperature of 70 °C). Thus, on the premise that sedimentation does not occur, the highest concentration of 2.5 wt% is selected.

Fig. 4a–d shows the surface and cross-section SEM micrographs of YSZ films prepared by repeating VD process different times using 2.5 wt% YSZ dispersion. As shown in Fig. 4a, one can see a dense YSZ film without any holes and cracks is obtained after five times of deposition and the average grain size is about 2–3 μm after a 1300 °C thermal treatment. As shown in Fig. 4b–d, the thickness of the YSZ films increases from 3.5 to 5.0 till 8.2 μm after depositing three, five, and eight times. Thus, increasing the repetition times of VD process significantly augments the thickness of YSZ films produced.

3.2. Electrochemical characterization

Open circuit voltage (OCV) is the voltage of a single fuel cell obtained at zero current that ranges from about 0.8 to 1.1 V. OCV is an important measurement for gas or electronic leakage through the electrolyte. A low OCV reduces the SOFC power output. Therefore, it is of great significance to test the OCV of a real SOFC device consisting of YSZ electrolyte prepared by VD method. Fig. 5a shows the relationship between the OCV of the single cells and the thickness of the YSZ electrolytes. The OCV of the real SOFC devices increases from 0.48 to 1.05 V as the thickness of YSZ films increases from 1.8 to 5 μm. The OCV of the single cell consisting of a 5 μm YSZ electrolyte reaches 1.05 V which is close to the theoretical value calculated by Nernst's equation. Fig. 5b shows that the OCV of the single cell remains stable at 1.05 V for 4 h at 700 °C. The results

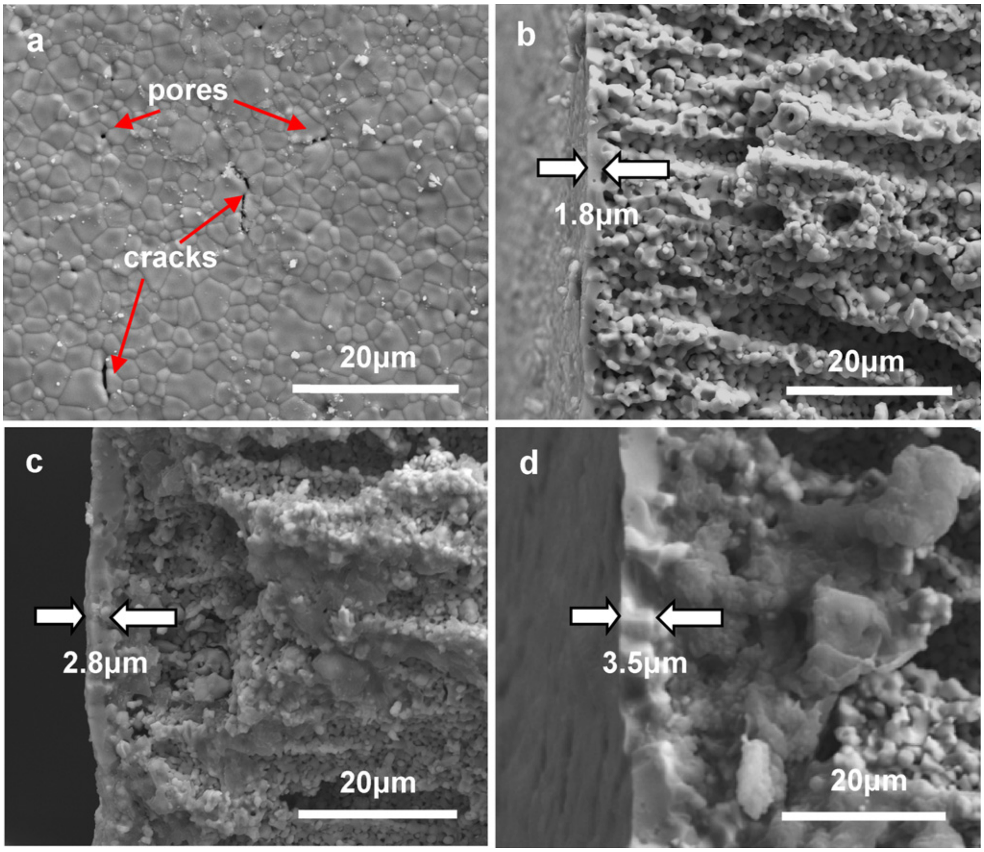

Fig. 3. (a) Surface and (b–d) cross-section SEM micrographs of YSZ films prepared by VD method using YSZ dispersions of different concentration. (a and b) 1.0 wt%; (c) 1.5 wt%; (d) 2.0 wt%.

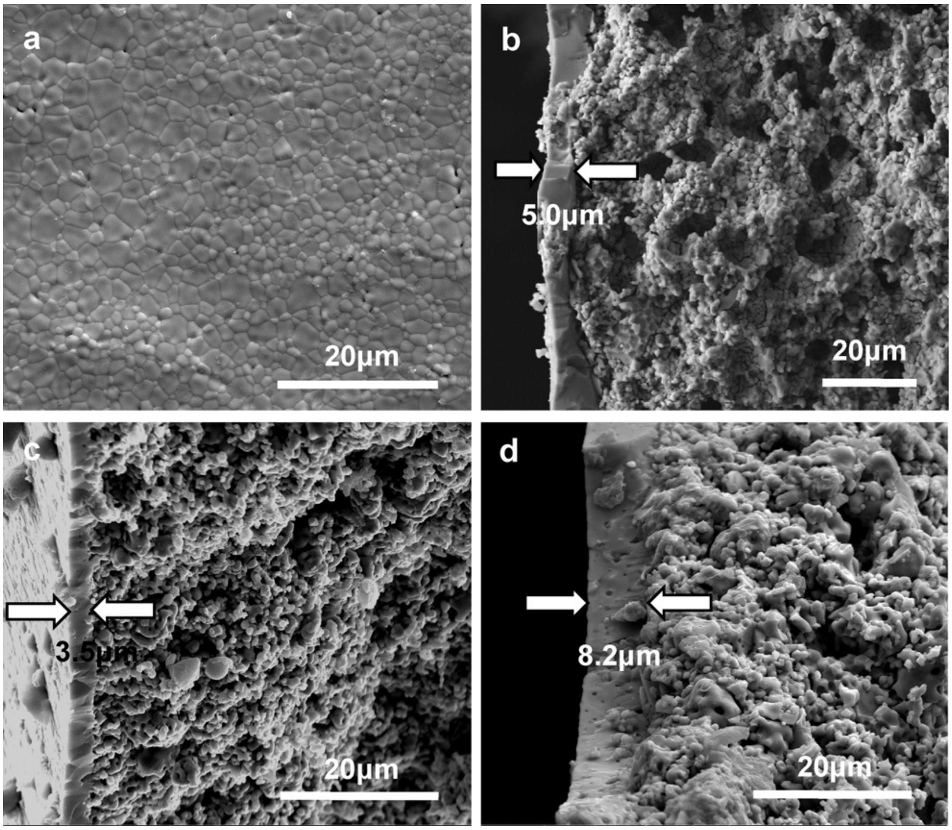

Fig. 4. (a) Surface and (b–d) cross-section SEM micrographs of YSZ films prepared by repeating deposition different times using 2.5 wt% YSZ dispersion. (a and b) Five times; (c) three times; (d) eight times.

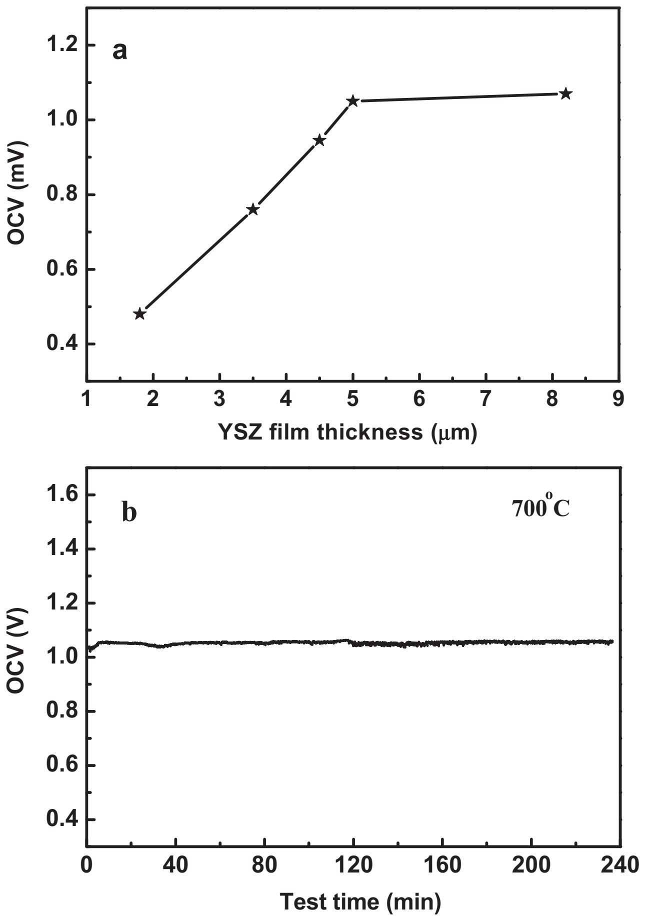

Fig. 5. (a) The relationship between the OCV of real SOFC devices and the thickness of the YSZ electrolytes; (b) OCV of the single cell consisting of a 5 μm YSZ electrolyte, as a function of holding time (at 700 °C).

indicate that when the thickness of YSZ electrolyte film is less than 5 μm, there are still via holes which result in the gas leakage and the reduction of OCV.

Shown in Fig. 6 is the typical performance of the single cell consisting of a 5 μm YSZ electrolyte prepared by VD method. The OCVs are all higher than 1.0 V in the testing temperature range from 650 to 800 °C. Such high OCVs certify that high quality YSZ electrolyte film has been obtained by sintering the vertical deposition YSZ film at the temperature as low as 1300 °C. The maximum power density is 0.4 W cm^{-2} at 800 °C which is equated to or even higher than the performance of the single cell reported by Jin et al. [27] using phase-inversion NiO–YSZ anodes.

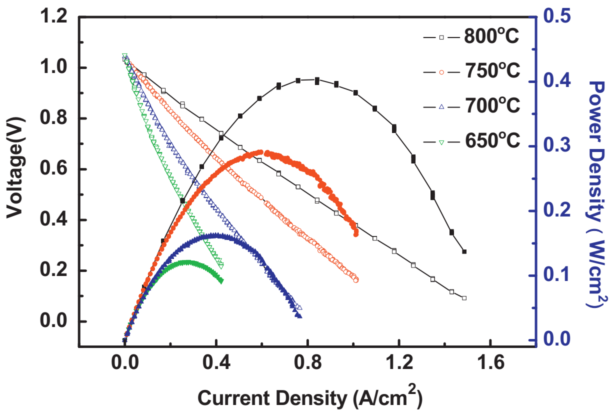

Fig. 6. I–V and I–P curves of the single cell consisting of a 5 μm YSZ electrolyte at 800 °C, wet hydrogen and ambient air are used as fuel and oxidant.

The above results suggest the feasibility of VD method for fabricating dense YSZ films on Ni-based anode supports. Further investigations concerning optimization of experimental conditions is required to realize the maximum benefits from VD method and further raise the power output of SOFC devices. Except for YSZ, other kinds of electrolyte films showing higher ionic conductivity are also potential to be prepared by VD method, extending its application in intermediate temperature SOFCs.

4. Conclusions

In this study, we introduced the facile and environment-friendly VD method to prepare dense YSZ thin films for application in SOFCs. As the concentration of YSZ dispersion and deposition times increase, the thickness of the YSZ films increases. A dense YSZ film which is 5 μm thick is successfully prepared by repeating deposition five times using 2.5 wt% YSZ dispersion. Electrochemical measurement on a real SOFC device consisting of a 5 μm YSZ electrolyte shows an open circuit voltage of 1.05 V at 700 °C and a maximum power density of 0.4 W cm^{-2} at 800 °C. The results suggest the feasibility of VD method for producing dense YSZ thin films. Compared with the conventional methods, VD method proposed herein shows the advantages of low cost, free use of organic reagents, and low sintering temperature.

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