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Fabrication and Characterizations of YSZ Electrolyte Films for SOFC

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Abstract: Yttria stabilized zirconia (YSZ) has been widely used as electrolyte in solid oxide fuel cell (SOFC). The effect of fabrication process on the properties of YSZ electrolyte thick film is discussed in the paper. With YSZ nano-powders of about 20-60nm as raw material, YSZ green adobe was fabricated by tape calendaring process. Three-step sintering process was performed firstly holding at 1000°C for 2h, then raising to 1300~1400°C, then decreasing to 1200~1300°C within 30 minutes, and finally calcining at 1200~1300°C for 5~20 hrs. Dense YSZs with relative density of 96-99% are obtained; the grain size of YSZ was reduced to 0.5-3µm. During the process of grain growth, there are both grain boundary diffusion and grain boundary migration. The feasibility of densification without grain growth relies on the suppression of grain boundary migration while keeping grain boundary diffusion active at a temperature as low as 1200~1300°C. Whereas the electric conductivities of the YSZs are even higher than that obtained in conventional single step sintering process. The process is applied to the anode-supported SOFCs co-fired at 1250~1300°C, and the cathode-supported SOFCs co-fired at 1200~1250°C.

Introduction

8mol% Yttria stabilized zirconia (YSZ) is the most popular electrolyte material in solid oxide fuel cell (SOFC) [1,2], in which the anode is Ni/YSZ and the cathode is doped lanthanum manganite (LSM)/YSZ. In electrolyte-supported SOFC, the thickness of YSZ electrolyte is generally 150 ~ 300 µm, which operates during 800~1000°C [3]. In electrode-supported SOFC, the thickness of YSZ electrolyte is generally 15~30µm, which operates during 600~800°C [3]. It is important for the three layers of Ni/YSZ-YSZ-YSZ/LSM to co-fire together in SOFC, which is helpful to reduce the inter-layer resistance and lower the manufacture cost. But, at present, the NiO/YSZ anode and YSZ electrolyte are co-fired during 1350-1450°C [4-7] and the YSZ electrolyte and LSM/YSZ cathode are required to co-fire during 1200-1250°C [8-12]. So, it is necessary to lower the sintering temperature of YSZ electrolyte to 1200-1300°C in order to co-fire the three layers of Ni/YSZ-YSZ-YSZ/LSM in SOFC. Because the thickness of YSZ electrolyte is generally 10~15µm in electrode-supported SOFC, the grain size of YSZ electrolyte layer is very important. However, due to higher surface energy of YSZ grains, YSZ grains tend to grow large in the sintering process [13]. Therefore, it is urgent to develop a novel sintering process for YSZ electrolyte films to obtain a desirable fine microstructure.

Materials and Methods

With the zirconium and yttrium nitrate hydrate (>99.99% pure, Baotou, China) as the cation sources, and ammonia (25%, A.R., Beijing, China) as the precipitation, the precursors for 8YSZ powders were precipitated first by dripping the salt solutions into an ammonia solution under mild stirring until pH≈8~9. Then the suspended solution was washed repeatedly with distilled water followed by drying at room temperature. Finally, the dried precursors were then calcined at 600~650°C for 2h [14].

The powders were characterized using HITACHI-H8100 TEM. The range of powder distribution was measured by SA-CP3 sedimentation centrifuge. The sintering behavior of the powders were analyzed by Netzsch Dil402C type thermal analyzer. The green adobes of YSZ with the thickness of 150-200 μm were made by tape calendaring process [TCL] with 30% polyvinyl alcohol (PVA) and 6% glycerine added into the powders [15]. The samples were punched into pellets with diameter of 20mm and thickness of 150-200 μm .

The YSZ electrolyte films were sintered at 1200-1300 $^{\circ}\text{C}$ in a high temperature box furnace (type-GXL-34/30/40). The density was measured according to Archimedes method. The grain size and microstructure were observed on SEM (GSM6700, Japanese). The electrical conductivity of YSZ electrolytes was measured via 4-probe DC technique. The AC impedance analyzer (Agilent 4294A) was used for the AC impedance measurement over the frequency range of 40Hz–110MHz.

Results and Discussion

Sintering process of YSZ. With the YSZ nano-powders as the raw materials, the grain size of YSZ powder is around 20~60nm, the mode diameter is 0.155 μm , the median diameter(d_{50}) is 0.153 μm and the d_{90} is 0.183 μm . The BET surface area is 15.2 m^2/g . The powders are uniform spherical and there are no hard agglomerates in them. These powders with uniform grain size and narrow grain distribution have the good sintering properties. The initial sintering temperature of YSZ powder is 990.5 $^{\circ}\text{C}$, which is relative to the grain size [16]. During the sintering processes, from 990.5 $^{\circ}\text{C}$ to 1400 $^{\circ}\text{C}$, the fastest sintering rate of the YSZ occurs at 1325.7 $^{\circ}\text{C}$, and the whole sintering process is completely finished at 1400 ~ 1450 $^{\circ}\text{C}$.

According to the sintering behavior of YSZ powders reported previously, three-step sintering process was pointed out for YSZ sintering. The temperature was raised at a rate of (60~100) $^{\circ}\text{C}/\text{h}$ from R. T. to 1000 $^{\circ}\text{C}$, then held at 1000 $^{\circ}\text{C}$ for 2 hours, then raised the temperature to 1300~1400 $^{\circ}\text{C}$ at a rate of 50 $^{\circ}\text{C}/\text{h}$ followed by rapid decrease to (1200~1300) $^{\circ}\text{C}$ and finally the furnace was held at (1200~1300) $^{\circ}\text{C}$ for 5~20 hours [17].

During the sintering process of YSZ, the first step is related to the nucleation of YSZ crystals at a temperature of about 1000 $^{\circ}\text{C}$. The YSZ nuclei are formed by surface diffusion, which overcomes the barrier of the surface energy [17]. There is an initial crystallite (nuclei) size d_c . Only those grains with the size of YSZ nuclei $d \geq d_c$ will grow in the later grain growth steps. Therefore it is necessary to hold a period of time (e.g. 2h) at about 1000 $^{\circ}\text{C}$, which helps to form a large number of nuclei with size larger than d_c [18,19]. These nuclei will grow in the following steps.

The second step in the sintering processes of YSZ, is related to grain growth at a temperature from 1000 $^{\circ}\text{C}$ to 1400 $^{\circ}\text{C}$ [17], because the grain growth needs a higher energy. The grain growth is associated with grain boundary motion, which is mainly controlled by grain boundary migration in higher energy state. The grain boundary migration would lead to grain growth quickly, so it is necessary to limit the time at the high temperature of 1400 $^{\circ}\text{C}$. The ideal process is that to lower the temperature to the required temperature in the range of 1200~1300 $^{\circ}\text{C}$ as soon as it reaches 1400 $^{\circ}\text{C}$. At this stage, the relative density of YSZ is about 80%.

The third step in the sintering processes of YSZ is related to densification behavior of the green body at lower temperature of 1200~1300 $^{\circ}\text{C}$ [17]. As we know, the grain growth behavior contains two processes: grain boundary diffusion and grain boundary migration. At relatively low temperature, according to Harmer and Brook [20], grain boundary diffusion may proceed; while at high temperatures, grain boundary migration becomes a dominant mechanism for grain growth. It is suggested that grain boundary migration may involve an activation process that needs higher activation energy than grain boundary diffusion. The feasibility of densification without grain growth relies on the suppression of grain boundary migration while keeping grain boundary diffusion active [21]. When the temperature is holding at 1200-1300 $^{\circ}\text{C}$, at which grain boundary migration is limited but grain boundary diffusion prevails. As a result, the YSZ grain size is limited in a certain range,

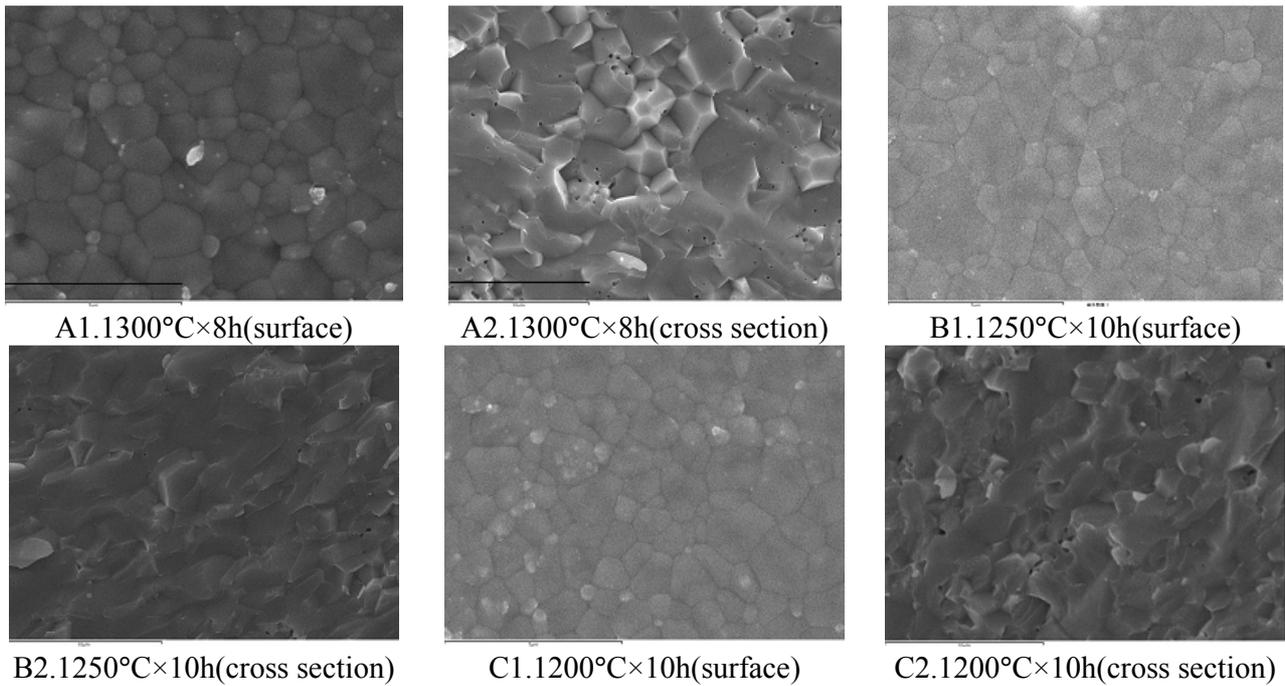


Fig.1 Microstructure of YSZ electrolyte sintered at 1200~1300°C

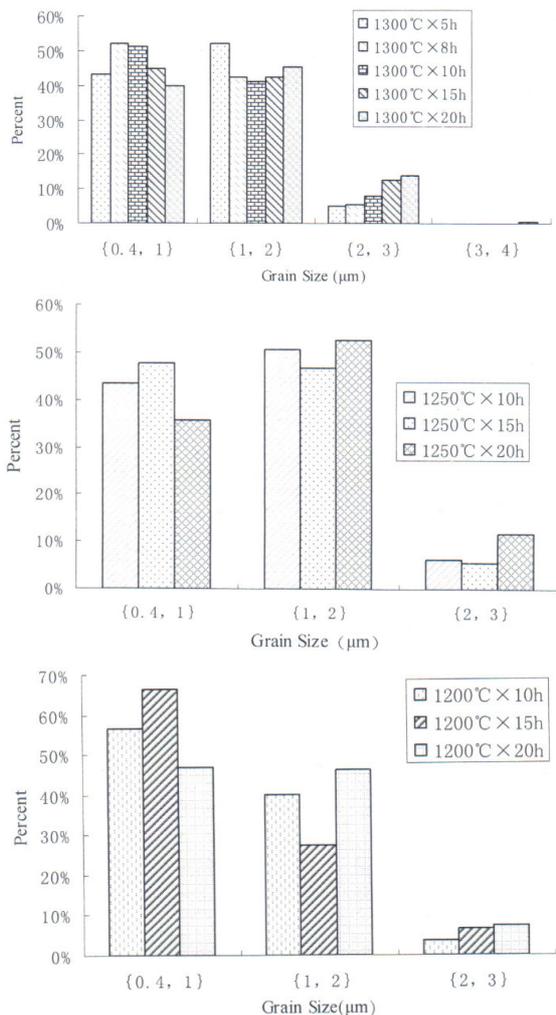


Fig.2 The grain size distribution of YSZ electrolyte sintered at 1200~1300°C

mostly below 1 μm . In this way, the YSZ grain size does not increase as dramatically as in conventional sintering method, but dense ceramic bodies are obtained. In order to ensure the sufficiency of grain boundary diffusion, relatively long time such as 10-20 hours are needed at 1200-1300°C. In the end, dense YSZs with the relative density higher than 96% were obtained.

Microstructure of YSZ films. The microstructure on surface and cross section of YSZ sintered at various conditions are shown in the Fig.1. In the dense YSZ samples, the grains are uniform and the grain boundaries are straight, clear and thin. From the surface microstructure, there are almost no pores. While from the cross section microstructure, a few pores are evident, some of which are inside the grains and others are in the grain boundary. The pores are minute and enclosed, which have little effect on the electrical conductivities of YSZ discussed later.

The grain size and size distribution of YSZ are shown in Fig.2. The size distribution of YSZ is in the range of 0.4~3 μm , most of them are less than 1 μm . At the same sintering temperature, the grain size becomes bigger when the holding time is longer. With the same holding time, the grain size increases with the sintering temperature increasing. There are three ranges of grain size: 0.4-1 μm , 1-2 μm , 2-3 μm . Only when sintered at 1300°C for 20h, there are a few grains bigger than 3 μm . In the YSZ samples sintered at 1200°C, the quantity of grain size below

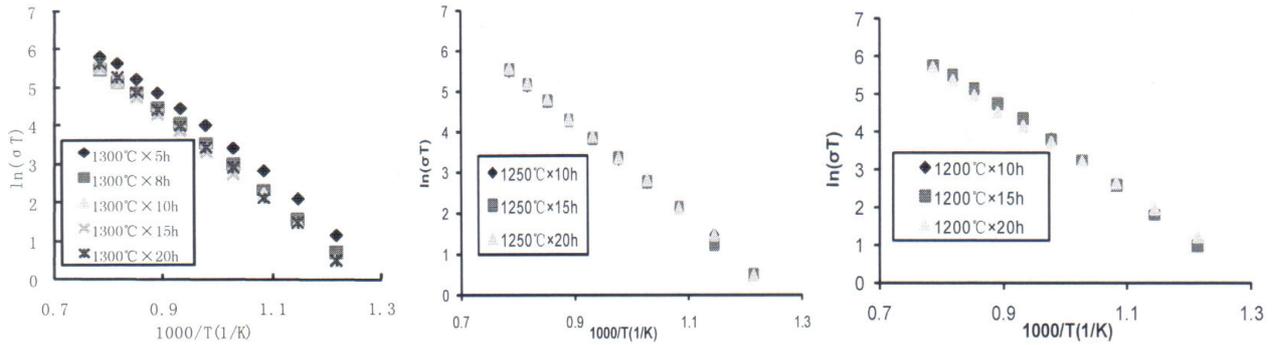


Fig.3 The electrical conductivity of YSZ sintered at 1200~1300°C

1 μm is more than 50%. The sub-micrometer grains in YSZ electrolytes are important to the electrode-supported SOFC, in which the desirable YSZ electrolyte films are less than 10 μm .

Electrical properties of YSZ. The electrical conductivities of YSZ prepared in different sintering processes are shown in Fig.3. It is indicated that the electrical conductivities are very similar. The electrical conductivities of YSZ at different temperature are higher than the report data [4].

When the grain size becomes smaller, the electrical conductivity does not decrease but becomes much higher. For dense ceramic solid electrolyte, the effect of pores is negligible. The conductivity of solid electrolyte is made up of grain conductivity and grain boundary conductivity. In view of traditional solid state ionic conductive theory, grain conductivity is two or three times higher than that of the grain boundary [22-24]. The properties of intergranular region play an important role in the overall conductivity of the electrolyte. The poor conductivity of the electrolyte is usually due to the low conductivity of the intergranular region. Many factors, such as grain size, intergranular area, impurity level and intergranular thickness, significantly affect on the apparent intergranular conductivity. It is suggested that there are two main reasons for low grain-boundary conductivity. Firstly, there is a space-charge layer near the grain boundary formed by solute segregation or a blocking layer for oxygen conducting formed by impurity phase. The other is that the conduction of oxygen ions decreases when the oxygen-vacancy concentration at the grain boundary is lower than in the grain interior [22].

In YSZ electrolyte, as YSZ grain size becomes smaller and smaller, the thickness of intergranular region decreases greatly. There are only several atom layers in the intergranular region, where there is hardly the solute segregation or impurity phase in the region to form the blocking layer for oxygen ion conducting. It is assumed that the oxygen-vacancy concentration at the grain boundary for oxygen ions conducting is not lower, but higher. So the intergranular conductivity would increase. Since the density is still high, the intragranular conductivity which is mainly depended on the density does not change significantly, as shown in Fig 8. Therefore, the total conductivity is improved.

In comparison of the electrical conductivities of YSZ sintered at different processes, the desirable sintering process is the 1200°C×10h, in which the electrical conductivities of YSZ are higher, i.e. 0.04s/cm at 800°C and about 0.2s/cm at 1000°C, than previously reported (0.006 600°C, 0.12s/cm at 1000°C [4]).

With the above low-temperature sintering process of YSZ, the electrode supported half cell could be made by co-firing processes [5]. In the anode-supported half cell, the Ni/YSZ cermet and YSZ were sintered together at 1250°C. The dense YSZ electrolyte film with a thickness of 15 μm coheres tightly with the porous matrix of Ni/YSZ cermet. The grain size of YSZ film is about 0.2-1.5 μm . In the cathode-supported half cell, the porous LSM/YSZ and YSZ were sintered together at 1250°C [11]. The thickness of the electrolyte is approximately 10~15 μm and the adhesion between the substrate and the electrolyte is good.

Conclusions

The sub-micrometer grain sizes such as 0.4-3 μm in YSZs are obtained by a three-step sintering process. The grain size became larger with the increase of temperature 1200~1300°C and holding time 5 ~ 20h. The grain size less than 1 μm is up to 65% when sintered at 1200°C for 15h, the largest grains from each sintering schedule is 2-3 μm , which is less than 10%. During the third sintering step at 1200~1300°C, the decreased temperature can suppress grain boundary migration but not affect grain boundary diffusion. As a result, the relative density is more than 96%, and the grain size in sub-micrometer range dominates. So the thickness of intergranular region decreases greatly, and there is not enough solute segregation or impurity phase in the region to form the blocking layer for oxygen ion conducting. Therefor the electrical conductivity is as high as 0.04s/cm at 800°C, and more than 0.2s/cm at 1000°C. The above result makes it possible to co-fire the anode-supported SOFCs at 1250~1300°C and the cathode-supported SOFCs at 1200~1250°C.

Acknowledgements

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