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Low cost fabrication and characterization of thin-substrate YSZ solid electrolyte

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Abstract

A new technique for the fabrication of yttria-stabilized zirconia (YSZ) substrates using aqueous gel-casting has been developed. This technique has been used to fabricate planar thin-substrate YSZ fuel cells. A thin-substrate YSZ electrolyte with high density and low porosity was prepared by this method with 57 vol.% solid content slurry. The character of the technique was discussed based on the influence of dispersant and pH value on slurry. After sintering, the YSZ electrolyte thickness is between 100 and 200 μm, and the electrolyte area is 100 mm × 100 mm. The research shows that aqueous gel-casting allows fabricate thin YSZ substrate with high density and homogenous structure. The method is suitable for preparing thin-substrate electrolyte of YSZ.

Keywords: Yttria-stabilized zirconia; Aqueous gel-casting; Thin-substrate

1. Introduction

The high operating temperature (∼1000 °C) of tubular solid oxide fuel cells (SOFCs) is necessary to attain reasonable power densities. However, a high operating temperature can introduce a number of complex materials problems, such as electrode sintering, interface diffusion between electrolyte and electrode materials, mechanical stresses due to the different thermal-expansion coefficients and high cost of ceramic interconnect materials. Thus, many recent major thrust in development are focused on planar SOFCs., which offer the potential of cheaper component production and assembly [1,2]. Cell-operating temperatures are reduced by using a thin-substrate YSZ electrolyte, and new electrode materials and designs to minimize cell-resistance and polarization losses [3].

Although the oxygen-ion conductivity of yttria-stabilized zirconia (YSZ) is not as high as that of other oxides such as doped ceria and doped lanthanum gallate, it is the preferred electrolyte due to its optimal combination of electrochemical and chemical stability and mechanical properties. Various attempts have been made to develop thin-substrate electrolytes using electrochemical deposition (EVD), plasma spraying, sol–gel methods, etc. A new technique for fabricating dense and thin-substrate YSZ electrolyte has been developed in our laboratory. Aqueous gel-casting is a near net-shape forming technique and is based on ideas borrowed from traditional ceramic processing and from polymer chemistry. It is a generic process which can be carried out readily in available equipment. Thus, it requires a minimum departure from conventional ceramic manufacturing practice.

Plasma spray and EVD techniques require high cost and complex equipments, meanwhile unlike sol–gel forming, in which the ceramic material is synthesized during the processing, aqueous gel-casting uses commercially available ceramic powder suspended in a solution of organic monomers. After casting, the solution is polymerized to form a strong, crosslinked, polymer-water gel filled with the powders. The polymerization permanently immobilizes the powder in the desired shape. Drying yields parts containing only about 3 wt.% polymer compared to about 30 wt.% binders in injection molding. In addition, dispersion of the powders in the gel-casting solution is an important process that must be controlled in order to produce a castable suspension with desirably high solid contents. The suspension pH is a critical parameter for this technique. Particles of zirconia interact

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with an aqueous solution and establish a surface charge that, if of sufficiently large magnitude, effectively counteracts the van der Waals forces that promote clustering, thereby providing electrostatic stabilization. The degree of surface interaction and the resultant surface charge depend on pH value [4].

2. Experimental

Sample powders were prepared as follows. YSZ powder (mean particle size of 3 μm) (Shenzhen Nanbo Corp., China) was commercially obtained. BET surface areas of YSZ was 6.0 m^2/g. YSZ slurries with dispersant (D3005, Rohm and Haas, USA) were prepared by thoroughly blending the desired amount of the oxide powders in water using a rotary-type partially stabilized zirconia ball mill for 15 h. The monomers used are monofunctional acrylamide (AM) and difunctional *N*,*N*′-methylene-bis-acrylamide (MBAM). The proportion of AM and MBAM is 20:1. The water soluble initiator and catalyst are ammonium persulfate ($(NH_4)_2S_2O_8$) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED), respectively. 5 wt.% $(NH_4)_2S_2O_8$ and 20 wt.% TEMED aqueous solutions were prepared.

The aqueous gel-casting process flow chart is shown in Fig. 1. After 8 wt.% water and 0.5 wt.% dispersant were added, the solution was mixed with 89 wt.% YSZ powder and milled to promote dispersion. The amounts of AM and MBAM reach 2% of total solution. The slurry was degassed in a rotary evaporator under vacuum until no further release of air bubbles was observed. Both 0.5 wt.% aqueous solution of ammonium persulfate and the catalyst, TEMED, were then added. The proportion of initiator and catalyst is 5:1. A glass mold was employed. After casting and gelation, both binder burnout and subsequent sintering were carried out in air [3].

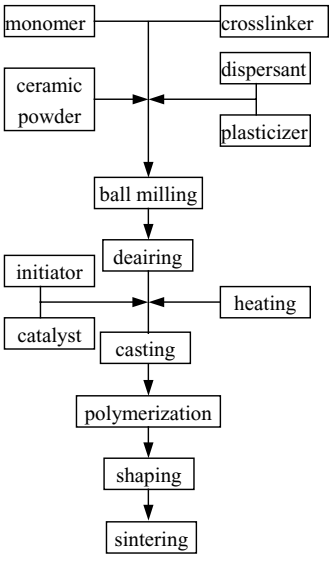

Fig. 1. Aqueous gel-casting process flow chart.

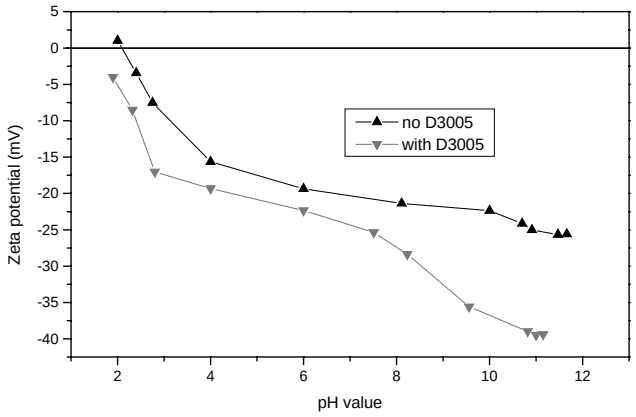

Fig. 2. Zeta potential vs. pH curves with and without surfactant addition, D3005 dispersant is polymer macromolecular electrolyte ammonium. Produced by Rohm and Haas company of USA.

The sintered sample was characterized by X-ray diffraction (XRD) using a Rigaku D/max IIIB with monochromater CuKα radiation. The relative densities of the sintered samples were determined through the Achimedes principle. Microstructures were observed by using a scanning electron microscopy (SEM). The sintered samples were cut into the shape of rectangles and four platinum-paste electrodes were fixed on them as current and voltage probes. Four probe direct current (dc) conductivity measurements were then performed on each sample at a range of temperature between 873 and 1473 K at about 100 K intervals.

3. Results and discussion

In order to improve dispersion, it is necessary to optimizing dispersant and adjusting pH value. A major portion of this work focused on increasing the charge on suspended particle surfaces as a means to improve dispersion and pH. As shown in Fig. 2, electrosteric surfactant additions were identified that increased surface charge of particles in the

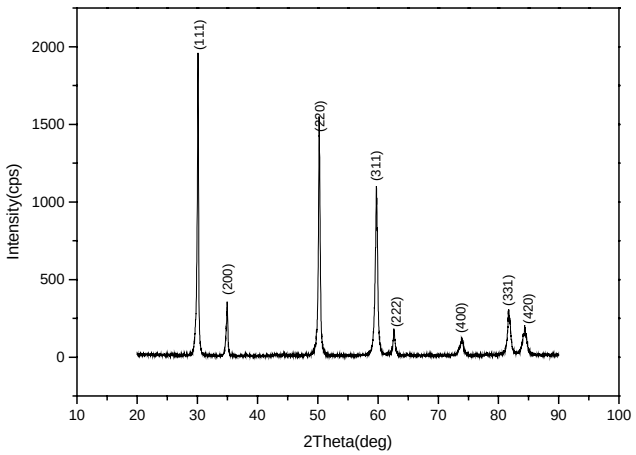

Fig. 3. The X-ray diffraction pattern of YSZ sample.

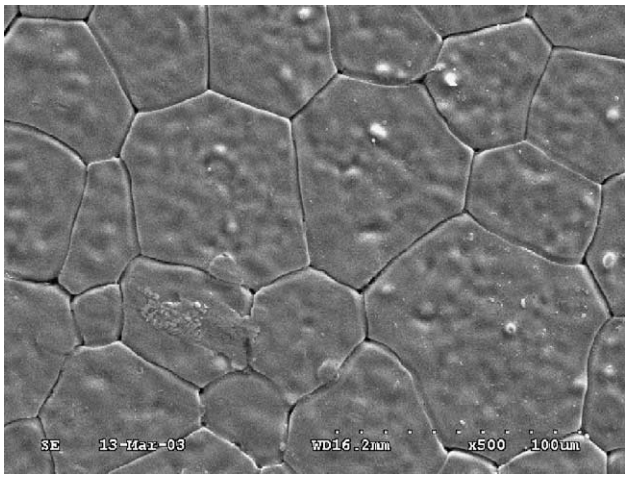

Fig. 4. SEM micrographs from the as received surface of YSZ sample.

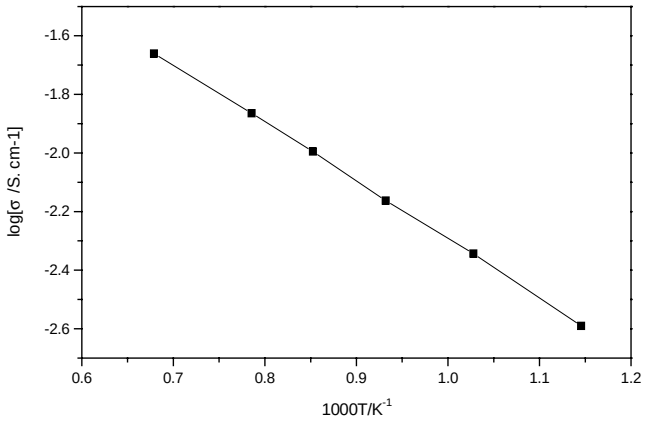

Fig. 5. Arrhenius plot for YSZ sample by four-probe direct current method.

suspensions of YSZ. These surfactants also extended the pH range of high particle surface so that dispersed suspensions can be prepared within high pH ranges. By applying these principles, YSZ suspensions of high solid contents and low viscosity were prepared in basic pH regimes [5].

The XRD patterns of YSZ sample are shown in Fig. 3. The data indicate the presence of mainly one phase, the cubic fluorite-type structure. Tetragonal and monoclinic zirconia phases are not found. Fig. 4 is the microstructure for YSZ sample. Fig. 4 shows a uniform grain distribution with a few isolated pores on the boundary, and straight boundaries higher density due to suitable sintering temperature (1500 °C) and holding time (2 h). The relative density of YSZ sample reaches 98% by Achimedes draining method.

Arrhenius plot of $\ln\sigma$ versus $1/T$ is shown in Fig. 5. dc conductivities are increasing with increasing temperature. The ionic conductivities measured at 1273 and 1473 K for YSZ sample are 0.155 and 0.190 S/cm, respectively. According to defect chemistry theory, in ZrO_2 based electrolyte, the charge carriers, the oxygen vacancies V_o are not free due to dopant cations to form defect associations at low temperatures [6]. Just about all the oxygen vacancies are free of association at an enough high temperature, so the YSZ sample can exhibit a higher conductivity when compared with low temperatures.

4. Conclusions

Dense thin-substrate YSZ electrolytes were successfully fabricated using aqueous gel-casting technique. Curve of zeta potential versus pH was changed with dispersant addition, and the charge of YSZ particle in suspension is increasing with increasing pH value. Only cubic phases were found in X-ray pattern of YSZ, and its ionic conductivity reaches 0.155 S/cm at 1273 K. It is suitable for electrolyte materials of SOFCs.

Acknowledgements

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