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Preparation of yttria stabilized zirconia membranes on porous substrates by a dip-coating process

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Abstract

Gas-tight yttria stabilized zirconia (YSZ, 8 mol.% Y_2O_3) membranes with expected composition were coated on porous ceramic substrates by a dip-coating process with YSZ sol, which was prepared by ultrasonic dispersion of YSZ powder in ethanol. The YSZ powder was synthesized by co-precipitation from inorganic aqueous solutions, followed by azeotropic distillation and sintering at 600°C for 2 h. The crystalline structure of YSZ powder was characterized by X-ray diffraction. Microstructures of YSZ membranes were analyzed by scanning electron microscopy and nitrogen permeation testing. The investigation showed that defects in the membranes could be gradually removed by repeating the dip-coating procedures. The electrical transport properties of the YSZ membrane were analyzed by AC impedance spectroscopy. The electrical conductivity of the membrane was 0.001 s cm⁻¹ at 900°C and the activation energy of electrical conductivity was found to be 87.5 kJ mol⁻¹. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Yttria stabilized zirconia; Sol-gel; Dip-coating; Ceramic membrane; Zirconia membrane

1. Introduction

The preparation of yttria stabilized zirconia (YSZ) membranes on porous substrates has received much attention recently. This is because YSZ is widely used as structural material due to a number of superior properties, including heat resistance, high hardness, chemical durability, and in the case of electrical applications using the oxygen ionic conductivity. Dense YSZ membranes are currently being applied in oxygen sensors and films for corrosion

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and heat resistance against oxidation, as well as solid oxide fuel cells. Porous YSZ membrane can be applied in the conventional liquid phase separations under harsh conditions and offer potential applications for high temperature catalytic reactions and gas separations. Besides, mesoporous YSZ membranes will find applications as supports for ultra-thin dense ceramic or metallic membranes.

Various attempts have been made to develop YSZ membranes on porous substrates using vapor deposition and wet processes. Among the wet processes, sol-gel chemistry is modified to deposit thin YSZ membranes onto porous substrates using different process routes. Chen et al. [1] deposited YSZ films on porous $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ and

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 $La_{0.8}Sr_{0.2}MnO_3$ by sol-gel processes using spincoating route with polymeric precursors. Films produced after 14 spin-coating cycles were observed to be dense by scanning electron microscopy.

Crack free porous YSZ membranes were reported by Okubo and co-workers [2,3] to be formed on porous YSZ substrate by a sol-gel process through controlled synthesis of zirconia sol, in which yttrium nitrate hexahydrate was dissolved. The formation mechanics of the crack free YSZ membranes were attributed to a networking model. However, elemental composition of X-ray photoelectron spectroscopy analysis showed that the YSZ membrane obtained was Y_2O_3 :Zr $O_2 = 0.06:0.94$ which was quite different with the starting conditions, Y_2O_3 :Zr $O_2 =$ 0.08:0.92. The reduction in the yttria content was interpreted as preferable transport of the free yttrium ion in the polymeric sol into the porous support.

In our earlier study [4] and a paper reported by Kim and Lin [5], porous YSZ films were deposited on porous alumina substrates with polymeric sol and particular sol, respectively. Analysis of the elemental composition was not reported. However yttrium contents should be lower than that expected since the ionic state of yttrium in these sols was Y^{3+} . No data were reported on electrical conductivity of the YSZ membranes in the above-mentioned work since the substrates were insulative.

In our present work, fine YSZ (8 mol.% Y_2O_3) particles are prepared and used as sol particles in order to get YSZ membranes with designed composition. A dip-coating route is applied to prepare the membranes on porous NiO–YSZ substrates, with which electrical conductivity of the membranes can be tested. The membranes are characterized by nitrogen permeation, scanning electron microscopy and impedance spectroscopy.

2. Experimental procedure

The sol-gel techniques used to prepare YSZ membranes in this work included three steps. Firstly, fine YSZ powder was synthesized. The powder was then used for producing a stable YSZ sol in ethanol. And finally, YSZ membranes were prepared with a dip-coating process.

2.1. Preparation of YSZ powder and sol

The starting solution, with a nominal composition ZrO_2 : $Y_2O_3 = 0.92$: 0.08 in molar ratio, was prepared from analytical-grade zirconyl chloride hydrate (ZrOCl₂.8H₂O) and yttrium chloride which were pre-standardized thermogravimetrically to confirm the actual cation composition. The materials were weighted in the defined molar ratio to yield a solution with a total cation concentration of 0.02 mol/l. Distilled water and ethanol with volume ratio of 1:1 was used as solvent. White precipitates were obtained by adding dropwise 0.1 mol/l ammonium hydroxide to the solution until pH = 8.0. The precipitates were filtered with vacuum suction and washed with distilled water three times to remove residual chloride ions. Further washing with ethanol was carried out three more times to remove most of the water. The filtered YSZ cake was then mixed with *n*-butanol, resulting in a suspension. The *n*-butanol was used to remove the residual water. The suspension was heated to boiling at about 93°C, the azeotropic point of water and *n*-butanol. After the water was carried out with butanol by azeotropic distillation, the butanol was evaporated at 117°C, the boiling point of *n*-butanol. After evaporation, the white powder was calcined at 600°C for 2 h to obtain YSZ structure. BET surface area of the YSZ powder was determined with a porosimeter (Micrometrics, ASAP 2000). The crystalline structure of the powder was characterized at room temperature by X-ray powder diffraction using a D/Maxra X diffractometer with Cu K_{α} radiation. The powder was then mixed in ethanol and ultrasonically dispersed to form a stable colloidal dispersion suitable for dip-coating YSZ membranes on NiO-YSZ substrates. The particle size of the YSZ sol was measured with an ALV/LSE-5000 Laser scattering sizer.

2.2. Preparation of YSZ membranes

YSZ powder, prepared by calcination of the precipitates at 900°C for 2 h, and nickel oxide (NiO) powder were mixed approximately as 45/55 wt.%, respectively. The powders were then cold-pressed under 2×10^8 Pa into cylindrical pellets of about 22 mm diameter and 2.5 mm thick. The green disks

were subsequently baked at 1400° for 5 h. Porosity of the sintered pellets was measured by the Archimedes method and found to be ~24%. Mean pore size of the sintered pellets was ~0.45 μ m, measured by bubble point method. YSZ films were prepared by dipping the supports for 10 s in the dipping sol, drying at room temperature for 2 h and calcining at a rate of 60°C/h to 1100°C, at which they were kept for 3 h. The dip-coating procedure was repeated until a gas-tight YSZ membrane was obtained.

2.3. Characterization of the films

The morphology evolution of the as-deposited films after annealing was investigated by a scanning electron microscope (SEM). Nitrogen permeation measurement was also applied to characterize the formation of YSZ membranes. The flux was measured with an in-house gas permeation system. To measure the electrical conductivity, electrodes consisting of platinum layers were baked onto the YSZ side of the pellets. The sample was heated at 700°C for 4 h in Ar + H₂ stream to reduce NiO to Ni. The resulting sample (Ni–YSZ/YSZ/Pt) was placed between platinum foil disks and spring loaded in quartz cells which were inserted in a tubular furnace with controlled temperature, under flowing argon. An AC impedance analyzer (GenRad 1689 RLC di-

gibridge), equipped with a micro-computer for data acquisition, was used to study the electrical conductivity of the YSZ film in the frequency range of 12 Hz–100 MHz. Pellets prepared by cold-pressing the dried YSZ powder and sintered at 1100°C for 3 h were used to compare the electrical transport properties of the YSZ membrane with those of the bulk materials.

3. Results and discussion

3.1. Characterization of YSZ sol

Room temperature X-ray diffraction (XRD) patterns are shown in Fig. 1. The dried precipitates had an amorphous structure before annealing. After calcination, it transformed into fluorite cubic structure, which is the typical structure of YSZ. The lowest temperature at which XRD data showed peaks corresponding to a crystalline phase was about 450°C. The XRD peaks for the powder heated up to 600°C are rather broad. The particle size in these materials estimated by XRD was of the order of 20 nm. After further heat treatment at 900°C and above, the powder became more crystallized. But the same diffraction pattern corresponding to cubic phase was observed in the sample. YSZ powder heated at 600°C



Fig. 1. XRD patterns of yttria stabilized zirconia (8 mol.% Y_2O_3) powder before calcination (a), after calcination at 600°C (b) and at 900°C (c) for 2 h.

for 2 h was used as the precursor of YSZ sol. As the YSZ powder was prepared by precipitation from an aqueous solution, the YSZ membrane formed with the sol had designed yttria content. Fig. 2 shows the particle size and its distribution of the YSZ sol. The data were obtained by laser scattering method. It can be seen that the sol had a narrow particle size distribution with mean radius of 116.0 ± 24.3 nm. The particle of YSZ sol is about five times larger than the crystalline size. Thus, it can be concluded that the YSZ particle in the sol is an aggregate of primary crystals rather than a single-crystalline par-



Fig. 2. Particle size distribution of YSZ sol obtained by laser scattering.

a

ticle. The BET surface area of the YSZ particles was 90.7 m^2/g .

3.2. Formation and microstructure of YSZ membranes

The dip-coating mechanism can be described as slip-casting [4,6]. When a porous substrate of Ni-YSZ is brought into contact with the YSZ sol, the solution gets into the substrate by capillary action. A YSZ layer was thus formed by concentration of the sol particles (YSZ) at the boundary of the support and the sol. The layer was converted to YSZ films after drying and sintering. Fig. 3a shows a crosssection of a YSZ membrane deposited on a NiO-YSZ substrate by the dip-coating procedure. The cross-section of the membrane after reducing NiO to Ni is shown in Fig. 3b for comparison. Fig. 3 shows that the YSZ film had good adherence to the substrate. It is difficult to identify, by SEM, the degree of permeation of YSZ particles into the substrate.

However, formation of cracks and defects could hardly be avoided during drying and sintering in the sol-gel process. In this work, densification due to sintering might be the main reason for crack formation. In order to remove the defects, the dipping procedure (dip coating, drying and sintering) was repeated several times. The nitrogen permeability of



Fig. 3. Scanning electron micrographs of the cross section of YSZ membranes (a) before being treated in H_2 -Ar stream at 700°C for 4 h (YSZ supported on porous NiO-YSZ) and (b) after treatment (YSZ supported on porous Ni-YSZ).



Fig. 4. Mean pressure dependence of nitrogen permeability through substrate and substrate with YSZ membranes from different dip-coating times.

the top layer was determined and if the membrane was not gas-tight, the system was dip-coated again, dried and sintered. Fig. 4 shows the nitrogen permeability as a function of mean pressure and the number of dip-coating procedures applied. Gas permeability test is usually applied to characterized membranes [4-6]. It is clear from this figure that nitrogen permeance decreases with the number of dip-coatings and after seven subsequent dip-coating procedures, the YSZ film is almost gas-tight. Nitrogen permeability after seven dip-coating procedures was less than 0.1% of that after the first dip-coating. Nitrogen flux could not be detected after 10 dipcoatings in this investigation. The gas-tight YSZ membranes could be applied to solid oxide fuel cells. Compared with vapor deposition techniques such as electrochemical vapor deposition, this fabrication technique has an advantage of lower cost [7].

The fact that the defects are removed by subsequent dip-coating procedures can be understood as a self-repairing mechanism. At the places where cracks and defects are present, the substrate is hardly or not at all covered with a YSZ film. Consequently, the solvent (ethanol) is easily transported at this place. During the next dip-coating procedure, ethanol permeates faster into the substrate at the defect site. This again implies that the YSZ layer growth is faster at the defect site than at other sites. Thus the cracks and defects are self-repaired. Fig. 5 indicates this self-repairing procedure. The SEM photograph of a YSZ film with many cracks is shown in Fig. 5a, from which it can be seen that the cracks are cross-linked with wideness of $2-3 \mu$ m. It can be estimated that about 30% of the area is not covered with YSZ film. After one more dip-coating, the crack depth became much smaller as can be found in Fig. 5b. The cracks are hard to distinguish after the third self-repairing as shown in Fig. 5c. And no cracks were visible under SEM investigation for a membrane after five more dip-coatings (Fig. 5d).

Models have been developed for ceramic membrane formation by dip-coating processes. In a recent reported model [8], the growth of film thickness L is interpreted as a function of substrate permeability (K_s) and permeability (K_m) of the film which is previously deposited

$$L = k \cdot \left(\frac{t \cdot \theta}{\alpha \left(\frac{1}{K_{\rm m}} + \frac{\alpha}{\theta \cdot K_{\rm s}}\right)}\right)^{1/2} \tag{1}$$

where θ is the substrate porosity, *t* is the dip-coating time, α is a constant related to sol concentration and film density and *k* is a function of the pore radius of the substrate, the viscosity and surface tension of the dipping sol. This equation can be rewritten by adding a constant *C* to account for a thin sol layer that



Fig. 5. Scanning electron microscopic photos of a YSZ membrane with many cracks (a), after the membrane was dip coated once (b), three times (c) and five times (d). The cracks are repaired step by step.

adheres to the substrate when the substrate is taken from the sol directly after dipping

$$L = k \cdot \left(\frac{t \cdot \theta}{\alpha \left(\frac{1}{K_{\rm m}} + \frac{\alpha}{\theta \cdot K_{\rm s}}\right)}\right)^{1/2} + C.$$
⁽²⁾

Places fully covered with a dense YSZ layer are impermeable to the ethanol. Thus $K_m \rightarrow 0$, and it holds that

 $L_1 = C. (3)$

For places where no YSZ is presented, Eq. (2) can be rewritten as

$$L_2 = \frac{k \cdot \theta}{\alpha} \cdot \left(K_s \cdot t\right)^{1/2} + C.$$
(4)

For places not fully covered with the YSZ layer, Eq. (2) could be expressed as follows under a reasonable assumption that the permeability of the substrate is much higher than that of the YSZ layer, that is $K_s \gg K_m$

$$L_3 = k \cdot \left(\frac{\theta \cdot K_{\rm m} \cdot t}{\alpha}\right)^{1/2} + C.$$
(5)

0.12

From Eqs. (4) and (5), with the assumption that $K_s \gg K_m$, and θ and α are constant, we obtain

$$\frac{L_2 - C}{L_3 - C} = \left[\frac{\theta \cdot K_{\rm s}}{\alpha \cdot K_{\rm m}}\right]^{1/2} \gg 1.$$
(6)

Thus the growth of the YSZ film on a partially covered place is much slower than that on an uncovered place. Meanwhile a partially covered place has a higher growth rate than a fully covered place, which can be easily understood from Eqs. (3) and (4). Eq. (3) describes the growth of a YSZ film on a fully covered area occurring after each dipcoating due to the adherence of the sol on the YSZ-covered area.

3.3. Electrical conductivity

Electrical conductivity of the gas-tight YSZ membrane obtained was measured as a function of temperature. The conductivity of a bulk YSZ made from dried powder and sintered at 1100°C for 3 h was measured for comparison. One arc was observed in the impedance spectra. The arcs obtained at 900°C for membrane and bulk materials are shown in Fig. 6. The left side intercepts of the extension line of the impedance arcs with the abscissa axis corresponded to the electrolytic resistance [9]. The electrical conductivity is shown in Fig. 7 as a function of reciprocal of the temperature of measurements. The conductivity of the YSZ membrane at 900°C was 0.001 S cm⁻¹. YSZ bulk material was much more conductive than membrane. The conductivity at 900°C was 0.05 S cm⁻¹. The bulk and membrane materials were different in porosity and electrode process. The effect of porosity and electrode processes on the electrical transport in ceramics could be characterized by impedance spectroscopy [9]. However, in the present spectra, separate arcs corresponding to bulk, grain boundary and porosity were not observed. The bulk YSZ had 78% theoretical density, and Pt-electrodes were applied to both sides of the YSZ pellet. However one electrode of the YSZ membrane was Pt, the other was porous Ni/YSZ composite. The membrane was gas-tight, but it could not be fully dense since the sintering temperature was much lower than that for the dense YSZ required [9]. The density of the membrane could not be

Fig. 6. Impedance spectra at 900°C of YSZ membrane and bulk materials.

measured in this work. However, the membrane should have a higher porosity than the bulk since the bulk sample was cold pressed before sintering. Activation energy for electrical conductivity was calculated from the slopes of the plots in Fig. 7. The activation energy of the membrane and bulk materials was 87.5 and 88.1 kJ mol⁻¹, respectively. The values are in the same range as in samples made by wet process [9]. Further research should be done on the dip-coating technique to increase the YSZ membrane conductivity.

4. Conclusion

Yttria stabilized zirconia sol with particle radius of 116.0 ± 24.3 nm was prepared by sonicated dispersing YSZ powders, which were synthesized from a





Fig. 7. Ln (σT) vs. reciprocal temperature 1/T for YSZ membrane and bulk materials, where σ is electrical conductivity S cm⁻¹ and T the absolute temperature.

co-precipitation and azeotropic distillation procedure. With the sol, YSZ membranes with expected Y_2O_3 content could be prepared by a dip-coating process. Defects such as pinholes and cracks could be self-repaired by repeating the dip-coating procedure. Crack-free (gas tight) YSZ membranes could be prepared by coating YSZ sol on the porous NiO–YSZ substrates more than 10 times. The gas-tight membrane was 10 μ m thick. Electrical conductivity of the membrane was 0.001 S cm⁻¹ at 900°C, which was much lower than the bulk material. The activation energy for electrical conductivity of the membranes was 87.5 kJ mol⁻¹.

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