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LETTER

Fabrication and microstructure of the $SrTiO_3$ composite membranes by Sol–Gel process

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Ceramic membranes, owing to their novel properties, are important materials widely used in separation, filtration, and catalytic reactions [1]. Ceramic membranes have several advantages over polymeric membranes such as better chemical and thermal stabilities, longer life, and better defouling properties. These properties have made ceramic membranes desirable for use in food, pharmaceutical and electronic industries, etc. [2]. Among several methods, the sol–gel approach is considered to be most practical one for the preparation of ceramic membranes because the smallest possible pore size is determined by the primary particle size in the colloid suspension [3]. Depending on the desired pore size of the membrane, the membrane precursor particles may be prepared by the sol–gel process [4]. The sol–gel process consists of a series of steps which are (i) hydrolysis of an organometallic compound, (ii) peptization, (iii) dipping, (iv) drying and (v) sintering. This technique allows high quality synthesis of ultrafine membranes. Titanium oxide membranes often show excellent chemical resistance as well as interesting photochemical and photocatalytic properties [5]. Titanium oxide membranes, however, could not be applied at high temperature (>500 °C) because of poor thermal stability. In the several studies related to the thermal stability of ceramic membranes, Burgfraaf et al. [6, 7] have determined the pore size of some ceramic membrane top layers at different sintering temperatures. This high thermal stability of the ceramic membrane allow it to be used in gas separation at high temperatures, especially in combination with a chemical reaction where the membrane is used as catalyst as well as a selective barrier to remove one of the components which has been formed [8–11]. In order to improve the thermal and physical properties of titanium oxide membranes, $SrTiO_3$ composite membrane was prepared by the sol–gel process. The effects of the strontium on the grain growth of $SrTiO_3$ composite membranes, pore size and mean particle diameter of the doped TiO_2 composite membranes are discussed in this study.

The process for preparing $SrTiO_3$ composite membranes by sol–gel process is schematically illustrated in Fig. 1. Titanium isopropoxide ($Ti(OC_3H_7)_4$) and Strontium Nitrate ($Sr(NO_3)_2$) were used as the starting materials. The titanium oxide sol was prepared by dissolving titanium tetraisopropoxide in isopropanol, followed by hydrolysis with excess water.

Dissociation of titanium sol requires addition of hydrochloric acid and the amount of acid added was derived from the solution pH. Reaction temperature of the slurry was kept at about 50 °C. The strontium solution was prepared by dissolving precursor in water. The additive solutions were prepared by dissolving the precursors in water. The additive solutions were mixed with the titanium oxide sol to form the mixed solutions. The mixed solutions were stirred thoroughly to give a homogeneous mixture. The tubular support was prepared by extruding from α -alumina with a mean particle size of 20–40 µm, followed by slip casting from α-alumina with a mean size of 0.3–10 µm. The multi-layer support was about 12 mm in outer diameter and about 2 mm in thickness. The multi-layer support was immersed in mixed sol for 5 to 60 s. The support with gel layer was dried for 48 h at 45 °C in the oven. The

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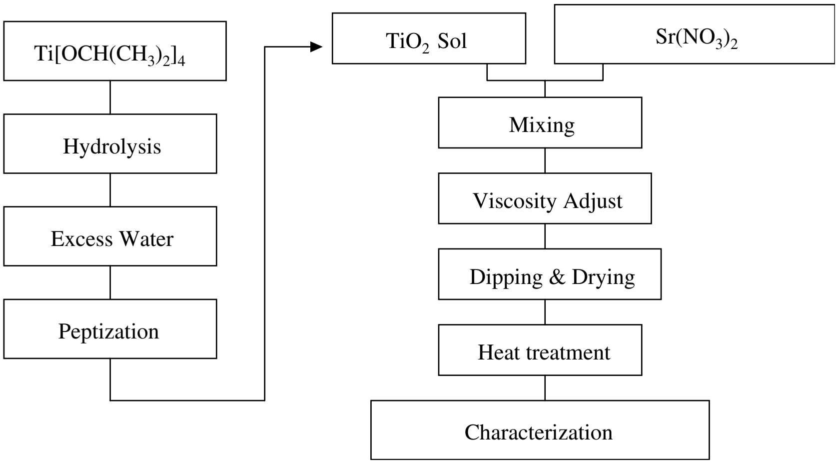

Fig. 1 Experimental procedure for synthesizing $SrTiO_3$ composite membranes by sol–gel process

support with thin film was calcined at 700 to 1100 °C for 1 h. The supported membranes were calcined at slow heating rate of 1 °C/min up to objective temperature and holding for 1 h, followed by cooling down to room temperature at a rate of 2 °C/min. The particle size and shape as well as the thickness of the membrane was observed with a scanning electron microscope (SEM, Hitachi S-4200). The particle size of the mixed sol was determined by using dynamic light scattering method (Ar laser, Nicomp 370). The viscosity of the sol was measured by using a viscometer (Brookfield, Mode DV-II).

Formation of a good gel layer depends greatly on the sol conditions used [12]. It is expected that the membranes having smaller pore diameter and narrower pore size distribution can be prepared from the sol whose particle size is smaller. A general feature of this technique is peptization, in which hydrolysis occurs without addition of any acid. Aggregates of primary particles form under these conditions. In order for formation of $SrTiO_3$ thin film, PVA solution was used to adjust the viscosity before mixed sols deposition on supports. The viscosity of the mixed sol was in the range of 12 to 35 cps at about 25 °C. The tubular support has particles typically of 20–40 μm and porosity around 40%. Figure 2 shows that the cross section of the synthesized $SrTiO_3$ composite membranes by sol–gel process. The thickness of the film was about 3 μm. The separation efficiency of inorganic membranes depends, to a large extent, on the microstructure features of the membrane/support composites such as pore size and its distribution, pore shape, porosity and tortuosity [13, 14] For efficient separations, porous inorganic membranes need to be crack-free and uniform in pore size. The microstructure change effect of the $SrTiO_3$ composite membranes with increasing heat treatment temperature have been investigated. It should be noted that addition of the strontium ions into the TiO_2 gel were conducted at the first stage of mixing two alkoxides, so that, after the sol–gel transformation, strontium ions should be distributed uniformly throughout the TiO_2 network. Figure 3 shows the surface microstructure of the $SrTiO_3$ composite membranes after calcining at 700 to 1100 °C for 2 h in air atmosphere. The average particle size of synthesized $SrTiO_3$ composite membranes was measured as a function of firing temperature. The mean particle size was determined by counting the number of particle size in a given area of the membrane. Whether it is a result of sintering or crystallization-induced, grain growth of $SrTiO_3$ was retarded by introducing the strontium ions into the TiO_2 membrane. The particle diameter of the $SrTiO_3$ composite membranes increased from 30 nm to 50 nm as firing temperature was changed from 700 °C to 900 °C. Under composite membrane increase was from 30 nm to above 100 nm. It is expected that the thermal stability of the TiO_2 composite membrane would increase by using the strontium ions component. The mean pore diameter of the $SrTiO_3$ composite membranes increase beyond the mesoporous region at temperatures higher than 600 °C for the pure TiO_2. This can be increased to above 900 °C for the strontium ion doped TiO_2 composite membranes. This increase in critical temperature is very important in the application of

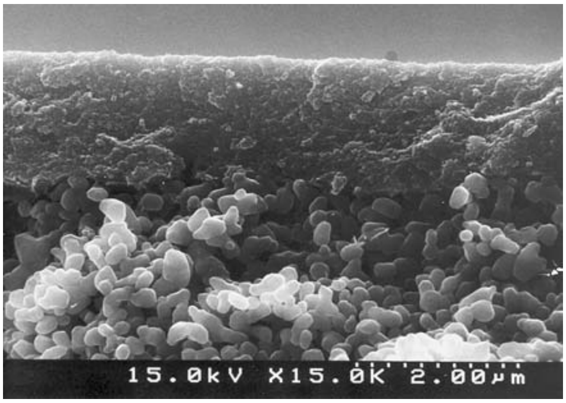

Fig. 2 Fracture surface of the supported $SrTiO_3$ composite membranes by sol–gel process

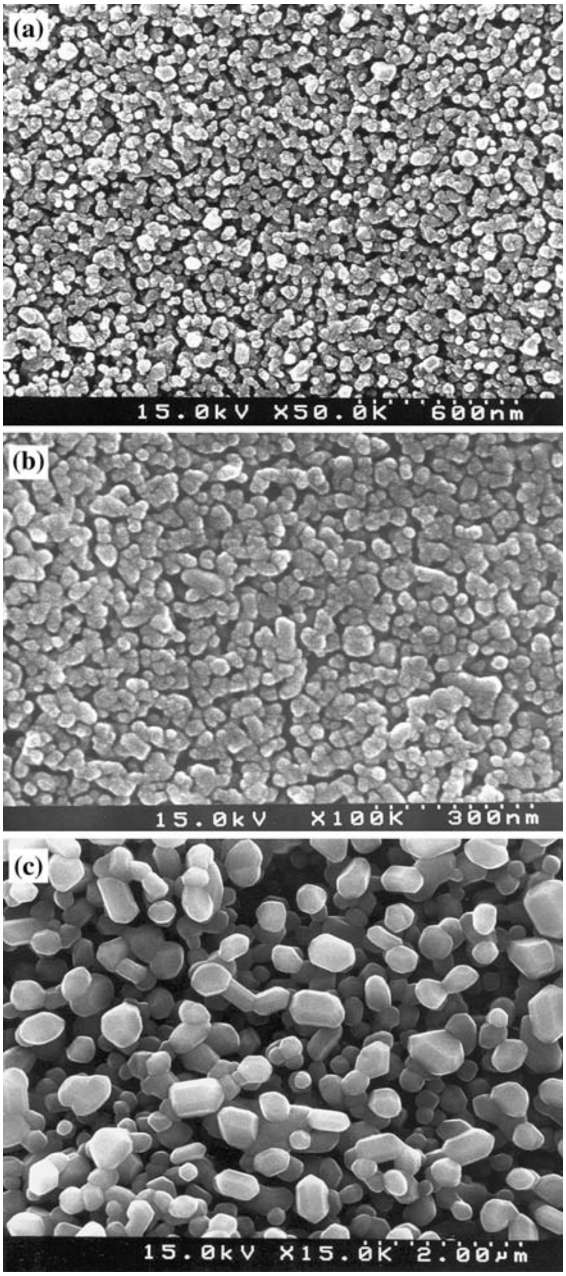

Fig. 3 Microstructure of the supported $SrTiO_3$ composite membranes as a function of heat treatment temperature for 2 h: (**a**) 700 °C, (**b**) 800 °C and (**c**) 1000 °C

mesoporous ceramic membranes in high temperature applications.

The supported $SrTiO_3$ composite membranes were prepared by dip-coating of a sol on an Al_2O_3 porous substrate. The mixed solutions were prepared by destabilization of colloidal solution process and the mean particle diameter of $SrTiO_3$ sols was below 30 nm in the pH of 1.12. A crack-free microstructure of the gel layer was obtained by drying at 45 °C for 48 h. The average pore size of synthesized $SrTiO_3$ composite membranes increased with increasing heat treatment temperature. The films demonstrated a narrow peak of mean particle diameter at around 30 to 40 nm after a heat treatment at 800 °C for 2 h. Whether it is a result of sintering or crystallization-induced, grain growth has been retarded by introducing the strontium ions into the TiO_2 membrane. The shape of the particles of the $SrTiO_3$ composite membranes became polygonal and the particle diameter distribution became broader with increasing heat treatment temperature (≥800 °C).

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