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Preparation and Properties of Perovskite-Dispersed Titania Membranes

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Abstract: Defect-free $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$ perovskite-dispersed titania (perovskite-titania) membrane was successfully prepared by sol-gel method combined with wet impregnation process. In this experiment, titania membrane was immersed in a perovskite solution, dried and calcined to obtain perovskite dispersed in titania membrane. The phase composition and membrane morphology of the membrane were characterized by thermogravimetric analysis (TGA), X-Ray Diffraction (XRD) spectroscopy, Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). The TEM result demonstrated that perovskite particles were well-dispersed among the titania particles. The SEM analysis showed that a uniform membrane approximately 0.5 μm thick on titania support was obtained after multiple coatings and calcination at 400°C. O_2 and N_2 permeability across the perovskite-titania membrane was measured to investigate membrane performance. From the permeability result, both gases appeared to decrease as the operating temperature increased, indicating that surface diffusion gradually reduced. The separation of O_2 from its binary mixtures containing N_2 was possible because the value of separation factor N_2/O_2 was slightly higher than the theoretical Knudsen diffusion.

Key words: Titania membrane, Perovskite, sol-gel method, characterization, morphology, gas permeability

INTRODUCTION

Titania is a well-known ceramic material employed in many industrial applications because of its superior physical and chemical properties. Titania membranes have been widely used in ultrafiltration processes, catalytic/photocatalytic membrane reactors, gas separations/reactions and gas sensing (Ahmad *et al.*, 2004; Tan *et al.*, 2007; Bayraktar *et al.*, 2007; Mohammadi *et al.*, 2007; Ding *et al.*, 2008; Wang *et al.*, 2008). In recent years, many papers have been published on the preparation of membranes derived from sol-gel method (Sekulic *et al.*, 2004), reversed micelle method (Ju *et al.*, 2002), chemical vapor deposition (Lin *et al.*, 1992) and anodic oxidation (Zhao *et al.*, 2005). In this study, sol-gel method is considered the most practical method. This method has demonstrated a homogenous microstructure and a feasibility to produce thin films on complex shapes when dip-coating is used; additional elements can also be added to further modify its properties (Pierre, 1998; Mohammadi *et al.*, 2007; Agoudjil and Benkacem, 2007).

Following the concept of a metal dispersed in a porous membrane, recent investigations have led to the development of metal-ceramic membranes such as zirconia/titania (Sekulic *et al.*, 2004), lanthana/titania (Sibu *et al.*, 2002) and silica/titania (Okada *et al.*, 2001). The abovementioned membranes were fabricated by

sol-gel method. In this light, the present study investigates the addition of perovskite particle dispersions within a titania layer formed over a macro-porous titania support.

A perovskite-dispersed alumina membrane was prepared by Irusta *et al.* (1998). The produced catalytic membranes were successfully used as combustors of volatile organic compounds contained in air streams. However, limited information exists about the synthesis and characterization of $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$ perovskite dispersed in titania membranes.

In study, therefore, the aim of this study is to develop and characterize perovskite-titania membranes. The titania layer was prepared by sol-gel method, whereas the coating of perovskite materials on the surface of the titania layer was conducted by the wet-impregnation process. Membranes were characterized by thermogravimetric analysis (Tga)/Differential Thermal Analysis (DTA), X-Ray Diffraction Spectroscopy (XRD), Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). Permeability of O_2 and N_2 across the perovskite-titania membrane was conducted to measure permeation performance of the membrane.

MATERIALS AND METHODS

Preparation of Titania membrane: Titania sol was prepared using titanium tetra-isopropoxide as a precursor

published elsewhere (Zaspalis *et al.*, 1992). A dipping solution for perovskite-titania membrane contained 30 mL 0.5 M titania sol mixed with 10 mL polyvinyl alcohol (PVA) solution at a concentration of 0.1 g per 100 mL and 20 mL hydroxypropyl cellulose (HPC) solution at a concentration 0.35 g per 100 mL. An adequate amount of dipping solution was coated onto a porous titania disc 20 mm in diameter and 2 mm in thickness by dip-coating method to form a supported titania membrane. Subsequently, the membrane was dried and calcined at 400°C for 2 h.

Perovskite was prepared by the same method detailed in a previous publication (Ahmad *et al.*, 2005). $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were weighed in equimolar amounts (0.025 mol) and dissolved in 0.036 L distilled water. The solution was stirred for approximately 1 h to ensure the mixture was dissolved and complete mixing was obtained. The perovskite phase was only obtained after the membrane was calcined at a higher temperature ($\leq 400^\circ\text{C}$). The type of perovskite obtained in this study was $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$.

Preparation of Perovskite-Titania membrane: In the Perovskite impregnation process, the titania membrane was immersed into Perovskite solution for 10 min. Subsequently, the membrane was dried and then calcined under air atmosphere at 400°C for 4 h. Finally, the Perovskite-titania membrane was obtained. The membranes were subjected to TG/DTA, XRD, TEM and SEM analysis.

Membrane characterization: The TG/DTA was performed using a thermogravimetric analyzer (Perkin Elmer TGA 7) to determine the burn out temperature of the organic additives and to examine calcination conditions. Phase transformation of the membrane during the calcination process was identified using an XRD (Philips PW1729 X-ray generator with Philips PW1820 diffractometer) with $\text{Cu K}\alpha$ radiation. TEM (Philips CM12) measurement was performed to investigate the dispersion of the particles in the solution. Membrane surface and thickness were observed under SEM (Leo Supra 50VP).

Gas permeability measurement: The experimental apparatus for gas permeability measurement is shown in Fig. 1. The permeability of the membrane (K) in $\text{mol.m/Pa/m}^2/\text{sec}$ is obtained using Eq. 1 (Li, 2007):

$$K = \frac{q_p t_m}{A_m \Delta P} \quad (1)$$

where, q_p is the gas flow rate from the permeate stream, t_m is the membrane thickness, A_m is the membrane's effective surface area and ΔP is the pressure difference between the feed and permeate streams.

Estimated membrane thickness based on SEM results was 500 nm. Thus, all membranes used in the permeation tests were assumed to possess a thickness of 500 nm. The separation factor of the membrane, $\alpha_{\text{O}_2/\text{N}_2}$, is equal to the

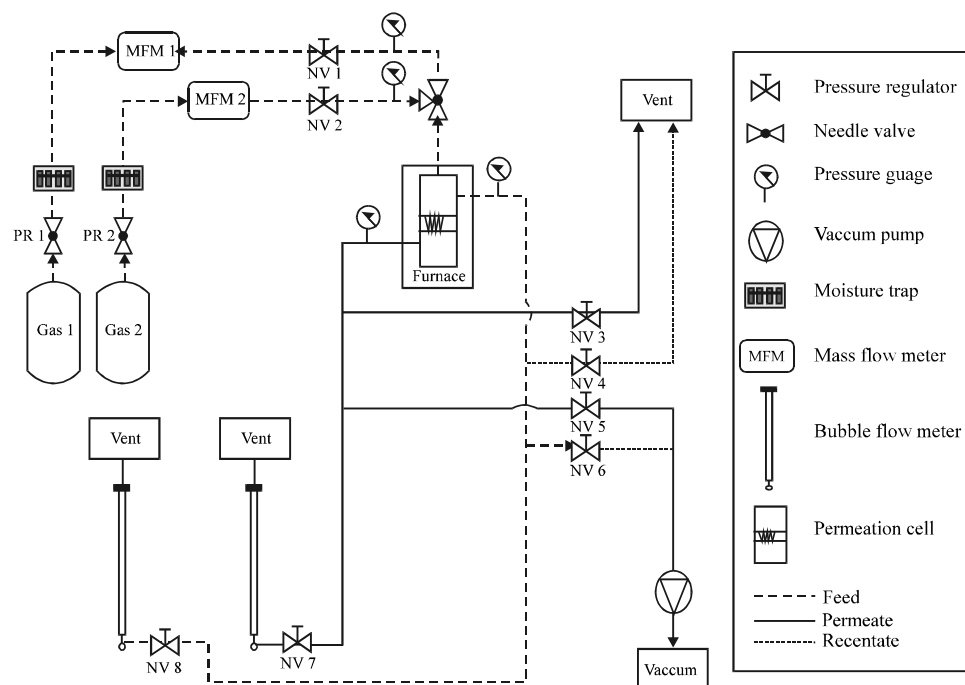


Fig. 1: Schematic diagram of the membrane permeation test rig

ratio of permeabilities between gases O_2 and N_2 under mixed gas feed conditions as shown in the following Eq. 2 (Li, 2007):

$$\alpha = \frac{K_{O_2}}{K_{N_2}} \quad (2)$$

The permeability of individual gases was conducted at the temperature range 28-350°C and an operating pressure fixed at 3 bars.

RESULTS AND DISCUSSION

Good membrane formation depends greatly on the condition of the sol used. Membranes having a smaller pore diameter and narrower pore size distribution could be prepared from a sol with small particle size (Bae *et al.*, 1998). Therefore, in this study, peptization ratio between nitric acid and metal (Ti^{4+}) concentration was adjusted to obtain stable sols with a minimum particle size. The peptization process was carried out at a ratio of 0.5, 1.0, 1.5 and 2.0. Optimal peptization ratio of H^+/Ti^{4+} was found to be 0.5 with 2 h of peptization process. These conditions were sufficient to yield a blue semi-opaque colloidal dispersion as the final product. Through observation, the resulting sol was stable and deflocculated evenly for several months. The titania sol also had small nano-sized particles with roughly spherical shape (Fig. 2). Its particle size ranged from 5-6 nm, unlike in the result reported by Zaspalis *et al.* (1992) using the same general method (30 nm).

The calcination temperature of titania membrane should ensure that organic additives (PVA and HPC) are completely decomposed and, at the same time, ensure that the membrane possesses an expected microstructure and a pure phase structure (Li *et al.*, 2009). To investigate the role of calcination temperature on the removal of organic content, as well as the temperature at which phase transformation from anatase to rutile phase occurred in the membrane during heat treatment, TG/DTA analysis was applied to the dried titania membrane gel (70°C dried for 24 h) to measure weight change in the heat flow as a function of temperature.

Figure 3a shows the DTA curve of a dried titania membrane gel that underwent endothermic dehydration in the temperature range 0-70°C, which is supported by a corresponding weight loss in the TGA curve. An exothermic small broad peak in the 70-125°C range shows the crystallization of the titania-anatase structure, whereas the next exothermic peak at 389°C shows the decomposition reactions of HPC and PVA (Mohammadi *et al.*, 2006a, b). An exothermic vast broad

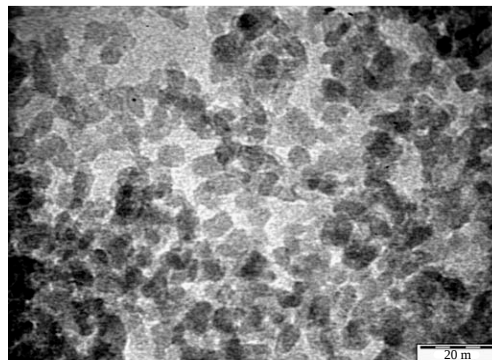


Fig. 2: TEM image of titania sol obtained by peptization of $Ti(OH)_4$ with nitric acid

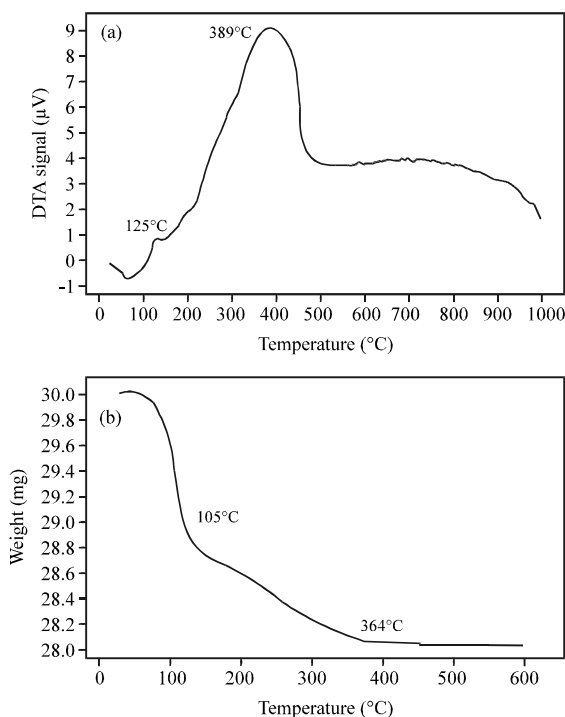


Fig. 3: (a) DTA and (b) TGA curve of the dried titania membrane gel with $3^\circ C \text{ min}^{-1}$ heating rate in air

peak in the temperature range of 500-900°C shows the gradual formation of the titania-rutile structure (Mohammadi *et al.*, 2006a, b).

Figure 3b shows the TGA curve of dried titania membrane gel. There are two regions of weight loss: that below 105°C and that between 120 and 364°C. In the first region, the weight loss of 0.7% is caused by the evaporation of physically absorbed water from pores (Kermanpur *et al.*, 2008). In the second region, the weight loss of 5.3% is caused by the combustion of HPC and

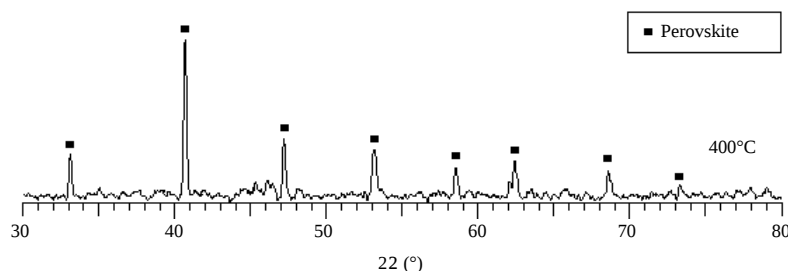


Fig. 4: XRD pattern of perovskite calcined at 400°C

PVA compounds and the crystallization from titanium hydroxide to oxide, which has been confirmed by DTA result (Mohammadi *et al.*, 2006a, b). There is no weight loss at temperatures above 364°C.

Results confirmed that the calcination temperature of titania membrane at 400°C was suitable for completely removing organic additives (HPC and PVA) and achieving pure anatase phase in the titania membrane.

Figure 4 shows the XRD pattern of perovskite calcined at 400°C. Results confirmed that the presence of a Perovskite structure readily occurred at 400°C (Rui *et al.*, 2009). Another major concern regarding the synthesis of perovskite is the presence of single-oxide phases, such as strontium oxide, ferric oxide and cobalt oxide. This phase can be the product of the incomplete oxidation process of perovskite. Careful analysis of the peak positions and intensities in the XRD pattern confirmed the absence of these compounds in perovskite. Therefore, results confirmed that perovskite type $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$ was obtained at 400°C.

The TEM images of the titania and perovskite-titania membrane calcined at 400°C is shown in Fig. 5a and b. In Fig. 5a, the titania membrane is shown to have small nano-sized particles with roughly spherical shape. The membrane was made up of particles with a mean size of 5.30 nm. Figure 5b shows that the perovskite crystals developed among the titania particles. The perovskite crystals were also composed of particles larger than the titania particles. Size of the perovskite particles ranged from 20-30 nm, whereas that of titania particles ranged from 5-10 nm.

Titania membrane was deposited by dip-coating technique on porous titania support. The dried membrane gel was calcined at 400°C and perovskite was then dispersed on the titania membrane by wet impregnation process. These two processes were repeated three times simultaneously. The SEM surface and cross-sectional images of the Perovskite-titania membrane's triple coating are shown in Fig. 6a and b, respectively. The surface area of the membrane showed homogenous dispersion of perovskite particles on titania layers without

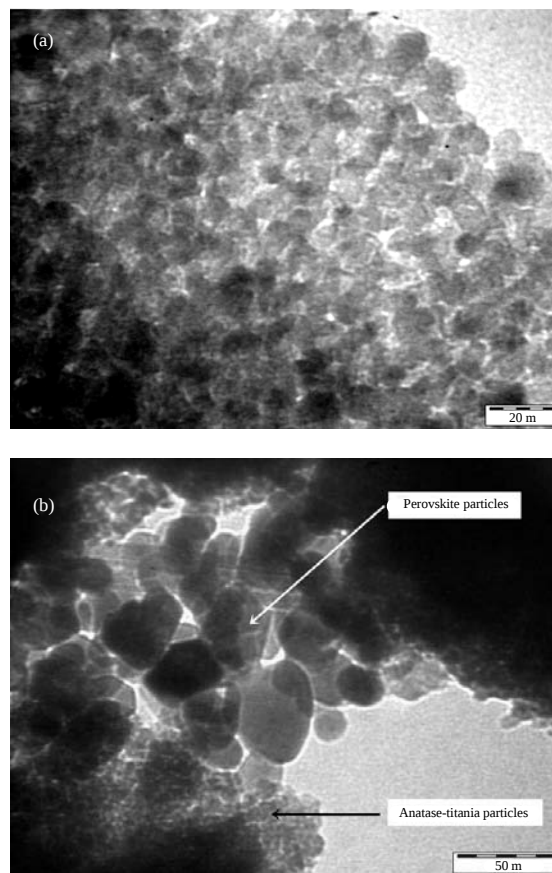


Fig. 5: TEM images of (a) titania membrane and (b) perovskite-titania membrane

cracking (Fig. 6a). The thickness of the Perovskite-titania membrane on titania support was estimated to be at approximately 0.5 μm . Multiple coating techniques can prevent crack formation and surface irregularities.

Figure 7 shows oxygen and nitrogen permeabilities across the perovskite-titania membrane as a function of the operating temperature. Permeability values of the gases calculated using Eq. 1 were nearly identical. Both gases appeared to decrease as the operating temperature

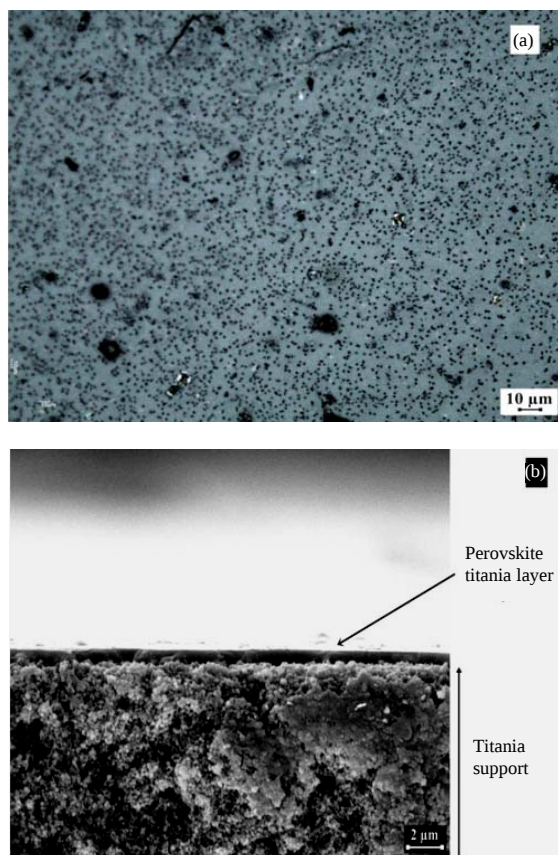


Fig. 6: SEM images of multiple-coated perovskite-titania membrane calcined at 400°C, (a) surface and (b) cross section

increased from room temperature to 350°C. The decreases were attributed to the gradual reduction in surface diffusion. The reduction of permeability due to surface diffusion was mainly attributed to the loading factor and surface diffusivity, which decreased at a higher temperature (Ahmad *et al.*, 2004). Generally, gas permeation mechanisms may be dominated by viscous flow, Knudsen diffusion, molecular sieving and surface diffusion and are strongly dependent on pore size and pore size distribution of the membrane, operating temperature and pressure, nature of the membrane and permeating molecules (Li, 2007; Mallada, 2008). The mechanism transport of this experiment dominantly involved Knudsen diffusion because the pore sizes of the membrane were in the mesoporosity regime (9.4 nm).

Figure 8 shows the separation factor of N_2/O_2 for perovskite-titania membrane as a function of operating temperature. In Fig. 8, the separation factor value for N_2/O_2 is about 1.12, as calculated from Eq. 2. The value was slightly higher than the theoretical Knudsen diffusion

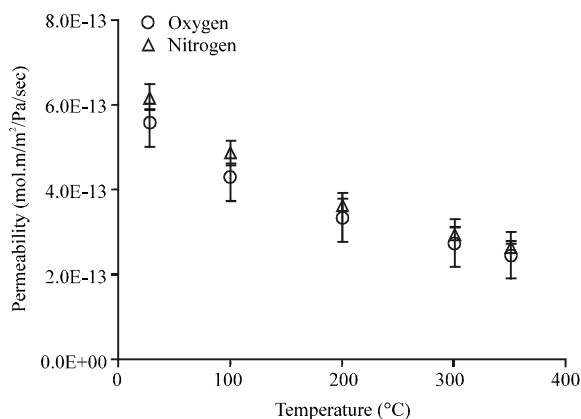


Fig. 7: Permeability of pure gases across perovskite-titania membrane

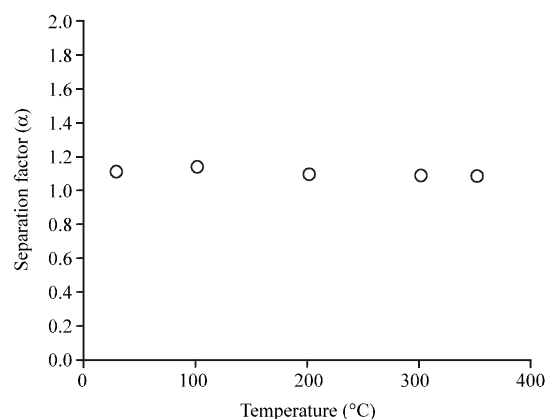


Fig. 8: Separation factor of O_2/N_2 across perovskite-titania membrane

(1.07), which is defined as the square root of the ratio of the heavier molecular weight gas (O_2) to the lighter molecular weight gas (N_2). The separation factor remained unchanged with increasing operating temperature possibly because the perovskite-titania membrane was able to retain its pore size at increasing operating temperature. Separation of O_2 from its binary mixtures containing N_2 was thus shown to be possible.

CONCLUSION

Titania-based membranes containing nano-perovskite dispersion was successfully prepared by sol-gel method combined with the wet impregnation process. TGA analysis showed that heat treatment at 400°C was sufficient to remove organic additives completely and to achieve pure anatase phase in titania membrane. The XRD analysis confirms the absence of single-oxide phases,

such as strontium oxide, ferric oxide and cobalt oxide in perovskite after being calcined at 400°C. A crack-free and homogenous surface area of perovskite-titania membrane was obtained after two processes of multiple coatings were applied. O₂ and N₂ permeability of the perovskite-titania membranes decreased as operating temperature increased. The mechanism of transport through the membrane dominantly involved Knudsen diffusion. The separation factor of O₂/N₂ was almost independent of the operating temperature and was slightly higher than theoretical Knudsen diffusion due to the ability of the membrane to retain small pore sizes.

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