

# Synthesis of a $\text{TiO}_2$ ceramic membrane containing $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$ by the sol–gel method with a wet impregnation process for $\text{O}_2$ and $\text{N}_2$ permeation

Abdul Latif Ahmad<sup>\*</sup>, Nur Aimie Abdullah Sani, Sharif Hussein Sharif Zein

*School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, Seri Ampangan, 14300 Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia*

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## Abstract

A  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  impregnated  $\text{TiO}_2$  membrane ( $\text{TiO}_2\text{--SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  membrane) was successfully prepared using a sol–gel method in combination with a wet impregnation process. The membrane was subjected to a single gas permeance test using oxygen ( $\text{O}_2$ ) and nitrogen ( $\text{N}_2$ ). The  $\text{TiO}_2$  membrane was immersed in the  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  solution, dried and then calcined to affix  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  into the membrane. The effect of the acid/alkoxide ( $\text{H}^+/\text{Ti}^{4+}$ ) molar ratio of the  $\text{TiO}_2$  sol on the  $\text{TiO}_2$  phase transformation was investigated. The optimal molar ratio was found to be 0.5, which resulted in nanoparticles with a mean size of 5.30 nm after calcination at 400 °C. The effect of calcination temperature on the phase transformation of  $\text{TiO}_2$  and  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  was investigated by varying the calcination temperature from 300 to 500 °C. X-ray diffraction spectroscopy (XRD) and Fourier transform infrared (FTIR) analysis confirmed that a calcination temperature of 400 °C was preferable for preparing a  $\text{TiO}_2\text{--SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  membrane with fully crystallized anatase and  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  phases. The results also showed that polyvinyl alcohol (PVA) and hydroxypropyl cellulose (HPC) were completely removed. Field emission scanning electron microscopy (FESEM) analysis results showed that a crack-free and relatively dense  $\text{TiO}_2$  membrane ( $\sim 0.75\text{ }\mu\text{m}$  thickness) was created with a multiple dip-coating process and calcination at 400 °C. The gas permeation results show that the  $\text{TiO}_2$  and  $\text{TiO}_2\text{--SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  membranes exhibited high permeances. The  $\text{TiO}_2\text{--SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  membrane developed provided greater  $\text{O}_2/\text{N}_2$  selectivity compared to the  $\text{TiO}_2$  membrane alone.

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## 1. Introduction

Ceramic membranes offer many advantages over polymeric membranes. They are stable at high temperatures, exhibit good chemical stability (especially in organic solvents) and have a high pressure resistance [1]. Ceramic membranes are superior for applications in gas separation, food and biotechnology, as well as in the filtration and treatment of water and waste water [2]. The ceramics that have been most extensively studied for membrane applications include  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{SiO}_2$ .  $\text{TiO}_2$  membranes have garnered considerable attention due to their high hydrothermal and chemical stability; good anti-fouling properties [3]; high surface reactivity to gases, which makes it suitable as a catalyst [4] and high specific surface area

for gas sensors [5]. Their potential applications include ultrafiltration processes, catalytic/photocatalytic membrane reactors, gas separations/reactions and gas sensing [6].

$\text{TiO}_2$  exists in a number of crystalline forms, the most important of which are anatase, rutile and brookite. Anatase and rutile are both tetragonal in structure, while brookite has an orthorhombic structure [7]. Anatase is the thermodynamically metastable form with respect to rutile, under all conditions of temperature and pressure [8]. The volume free energy of the rutile phase is always lower than that of the anatase phase. Therefore, heat treatment transforms the anatase phase to the stable rutile phase. The temperature of the transformation depends heavily on the nature and structure of the precursor and on the preparation conditions. Most of the chemical preparation methods yield  $\text{TiO}_2$  in the metastable anatase phase and shift it to the rutile phase after further heat treatment [9,10].

The perovskite-type oxide,  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$ , is a typical mixed ionic electronic conducting membrane material that has

<sup>\*</sup> Corresponding author. Tel.: +60 4 593 7788x6414; fax: +60 4 594 1013.  
E-mail address: [chlatif@eng.usm.my](mailto:chlatif@eng.usm.my) (A.L. Ahmad).

drawn a significant amount of attention and has been applied in the chemical and petroleum industries. Presently, the use of  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  as an  $\text{O}_2$  separation membrane has been considered because of its higher oxygen ion and electron conductivity.  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  can also operate steadily for longer durations at high temperatures [11]. A  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  membrane is usually used alone and is prepared using a conventional solid state method to form a  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  powder. This powder is compressed into a disc and sintered before application in gas-separation processes [12].

To the best of our knowledge, there are no reports on the preparation of  $\text{TiO}_2$  membranes containing  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$ , especially using the sol–gel method in combination with a wet impregnation process. Therefore, this paper reports the synthesis of  $\text{TiO}_2$ – $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  membranes for  $\text{O}_2$  and  $\text{N}_2$  permeances. The  $\text{TiO}_2$  membrane was prepared by a sol–gel method and  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  was affixed to the  $\text{TiO}_2$  membrane using a wet impregnation process. The membranes were characterized using transmission electron microscopy (TEM), XRD, FESEM and FTIR. The membrane developed was tested on  $\text{O}_2$  and  $\text{N}_2$  gases and the  $\text{O}_2/\text{N}_2$  selectivity across the  $\text{TiO}_2$  and  $\text{TiO}_2$ – $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  were documented.

## 2. Methodology

### 2.1. Preparation of membrane support and binders

A porous  $\text{TiO}_2$  disc (prepared from titanium (IV) oxide powder) was used as a membrane support for a  $\text{TiO}_2$ – $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  membrane. The support had a 20-mm diameter and 2-mm thickness. About 1.75 g of  $\text{TiO}_2$  powder was loaded into the stainless steel mold. The mold was then pressed using hydraulic press equipment up to 20 MPa pressure. After pressing, the support was dried at 70 °C, followed by a calcination process at 965 °C for 4 h. To prevent cracking of the support surface, the heating and cooling rate employed during the calcinations was 2 °C/min.

Polyvinyl alcohol (PVA) and hydroxypropyl cellulose (HPC) were used as binders to prevent the formation of cracks on the thin membrane surface. They were also used to affix the  $\text{TiO}_2$ – $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  membrane to the membrane support. The PVA solution was prepared by dissolving 0.1 g of PVA into 100 ml distilled water, followed by stirring for approximately 1 h. The HPC solution was prepared by dissolving 0.7 g HPC into 100 ml distilled water and stirring for 1 h.

### 2.2. Preparation of $\text{TiO}_2$ sol

The sol–gel method was used to prepare the  $\text{TiO}_2$  sol. The starting materials for the preparation of the  $\text{TiO}_2$  sol were the following: (1) titanium tetraisopropoxide (TTIP) as the  $\text{TiO}_2$  precursor, (2) nitric acid as the catalyst for the peptization, (3) distilled water as the dispersing medium and (4) isopropanol as the solvent.  $\text{TiO}_2$  sol was prepared by hydrolysis of TTIP. A solution of TTIP in isopropanol (0.45 M) was added drop wise into a solution of isopropanol (4.5 M) in distilled water under vigorous stirring. After the hydrolysis reaction was complete,

the remaining white precipitate of titanium hydroxide ( $\text{Ti}(\text{OH})_4$ ) was filtered and washed with water to remove the alcohol. The filtrate was then dispersed in distilled water ( $\text{Ti}^{4+}$ ) and nitric acid was added to achieve a 0.5 molar ratio of acid/alkoxide ( $\text{H}^+/\text{Ti}^{4+}$ ). The process was repeated with the following ratios: 0.5, 1.5, 2.5 and 3.5. Next, the solution was peptized for 2 h at 70 °C. A closed beaker was used to enhance the rate of peptization. To break the weak bonds of the agglomerated particles, the sol was treated ultrasonically for 30 min. The final product was a blue, semi-opaque colloidal dispersion at a concentration of 0.325 M. A dilute concentration of the dispersion was produced by dilution with distilled water.

### 2.3. Preparation of the $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$ solution

$\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  was prepared as described in a previous publication [13].  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  were weighed in equimolar amounts and dissolved in distilled water (0.7 M). The solution was stirred for approximately 1 h to ensure that it was completely dissolved. The  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  phase was obtained after the membrane was calcined.

### 2.4. Preparation of the $\text{TiO}_2$ – $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$ membrane

The  $\text{TiO}_2$  membrane was created from the  $\text{TiO}_2$  sol. The  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  was then affixed within the  $\text{TiO}_2$  membrane pores using a wet impregnation process.

The dipping solution for the  $\text{TiO}_2$  membrane contained 30 mL 0.05 M  $\text{TiO}_2$  sol mixed with 10 mL PVA solution and 20 mL HPC solution. An adequate amount of dipping solution was used to coat the membrane support by dip-coating to form the supported  $\text{TiO}_2$  membranes. The membranes were then dried and calcined at different temperatures (100, 300 and 400 °C) for 2 h. The membranes were screened using TEM and FTIR analysis and evaluated for membrane performance.

For the  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  impregnation process, the  $\text{TiO}_2$  membrane was immersed in a  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  solution for 10 min. The membrane was then dried and calcined under atmospheric air at 400 °C for 4 h. The  $\text{TiO}_2$ – $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  membrane was tested using XRD and FESEM analyses and evaluation of membrane performance was conducted.

### 2.5. Membrane characterization

TEM (Philips CM12) was performed to investigate the dispersion of the particles in the  $\text{TiO}_2$  sol. The phase transformation of the membrane during the calcination process was identified using XRD (Philips PW1729 X-ray generator with Philips PW1820 diffractometer) with  $\text{Cu K}\alpha$  radiation. The surface and thickness of the membrane were observed using FESEM (Leo Supra 50VP). FTIR analysis was performed using the FTIR 2000 Perkin Elmer spectrophotometer and the samples were prepared using a KBr pellet.

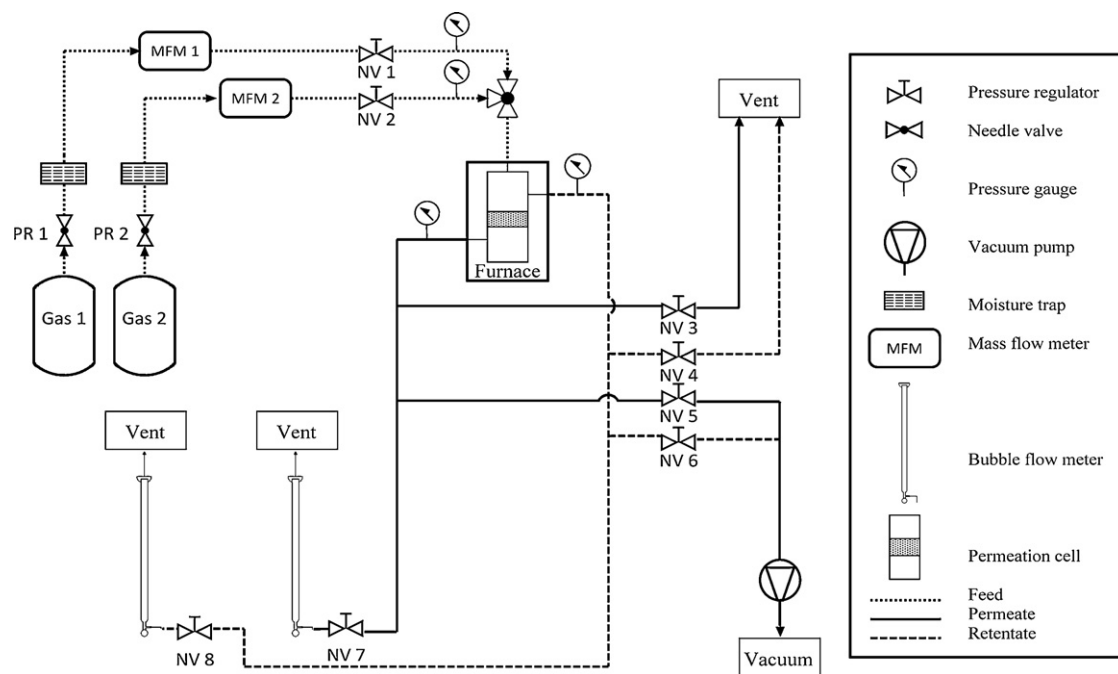


Fig. 1. Schematic diagram of the membrane gas permeation test rig.

## 2.6. Gas permeation measurement

The experimental apparatus utilized for the gas permeation measurements is illustrated in Fig. 1. Single-gas permeance was determined for O<sub>2</sub> and N<sub>2</sub>, and the ideal selectivity was defined as the ratio of their permeances. The permeance of the membrane ( $K$ ) in mol/m<sup>2</sup> Pa s was obtained using Eq. (1) [14]:

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

where  $q_p$  is the gas flow rate of the permeate stream,  $A_m$  is the membrane's effective surface area and  $\Delta P$  is the pressure difference between the feed and permeate streams. The ideal selectivity of the membrane,  $\alpha_{O_2/N_2}$ , is equal to the ratio of permeances between O<sub>2</sub> and N<sub>2</sub>, as shown in Eq. (2) [14]:

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

The permeance of the individual gases was determined in the temperature range of 28–350 °C and at a fixed operating pressure of 3 bars.

## 3. Results and discussion

### 3.1. Effect of the H<sup>+</sup>/Ti<sup>4+</sup> molar ratio on the TiO<sub>2</sub> phase transformation

In this study, nitric acid was used as the peptizing agent. The TiO<sub>2</sub> membrane properties were studied at several H<sup>+</sup>/Ti<sup>4+</sup> molar ratios, ranging from 0.5 to 3.5. This study was conducted in the absence of PVA and HPC. Fig. 2(a)–(d) shows the TEM images of the TiO<sub>2</sub> membrane after calcination at 400 °C at different H<sup>+</sup>/Ti<sup>4+</sup> molar ratios. The TiO<sub>2</sub> sol created at a 0.5

molar ratio had the smallest-sized nanoparticles, of roughly spherical shapes (Fig. 2(a)) and a mean size of 5.30 nm, which is in contrast to the result reported by Zaspalis et al. [15] using the same general method (30 nm). Similar trends were reported by Gestel et al. [3] and Alem et al. [16]. However, the nanoparticle size in the TiO<sub>2</sub> sol increased as the H<sup>+</sup>/Ti<sup>4+</sup> molar ratio increased from 0.5 to 3.5, while this increase in molar ratio decreased the pH value from 1.3 to 0.3 (Table 1). A decrease in pH is believed to favor anatase over rutile transformation [17].

During the peptization process, H<sup>+</sup> ions from the nitric acid are adsorbed by the surface of the sol particles. The ions repel each other to form a stable colloidal sol. This electrostatic repulsion also prevents particles from sticking together and forming aggregates [18]. Peptization with acid leads to the breakup of large aggregates into nanoparticles by the electrostatic repulsion of the charged particles. Nanoparticle sols produced gels with efficient particle packing, while aggregated sols produced gels with a much more open structure, higher porosity and a larger pore size. The anatase phase has been found to have an isoelectric point (pH<sub>iep</sub>) that ranges from 4.7 to 6.7. At a pH well below the pH<sub>iep</sub> (e.g., pH = 1–2), the surface of TiO<sub>2</sub> would have a net positive charge, yielding nanoparticle sol [7]. Formation of small pore size and crack-free membrane heavily depends on the condition of the utilized sol. It has been shown that membranes with a smaller pore diameter and a narrower pore size distribution can be made from a sol of nanoparticles [19].

Fig. 3 shows the XRD patterns of the TiO<sub>2</sub> membrane with different H<sup>+</sup>/Ti<sup>4+</sup> molar ratios and a calcination temperature of 400 °C. The findings indicate that the TiO<sub>2</sub> sol with a 0.5 molar ratio exhibits an amorphous anatase phase as the dominant XRD peak at  $2\theta = 25.3^\circ$ , whereas an increased molar ratio of TiO<sub>2</sub> sol shows a partial rutile phase transformation. The

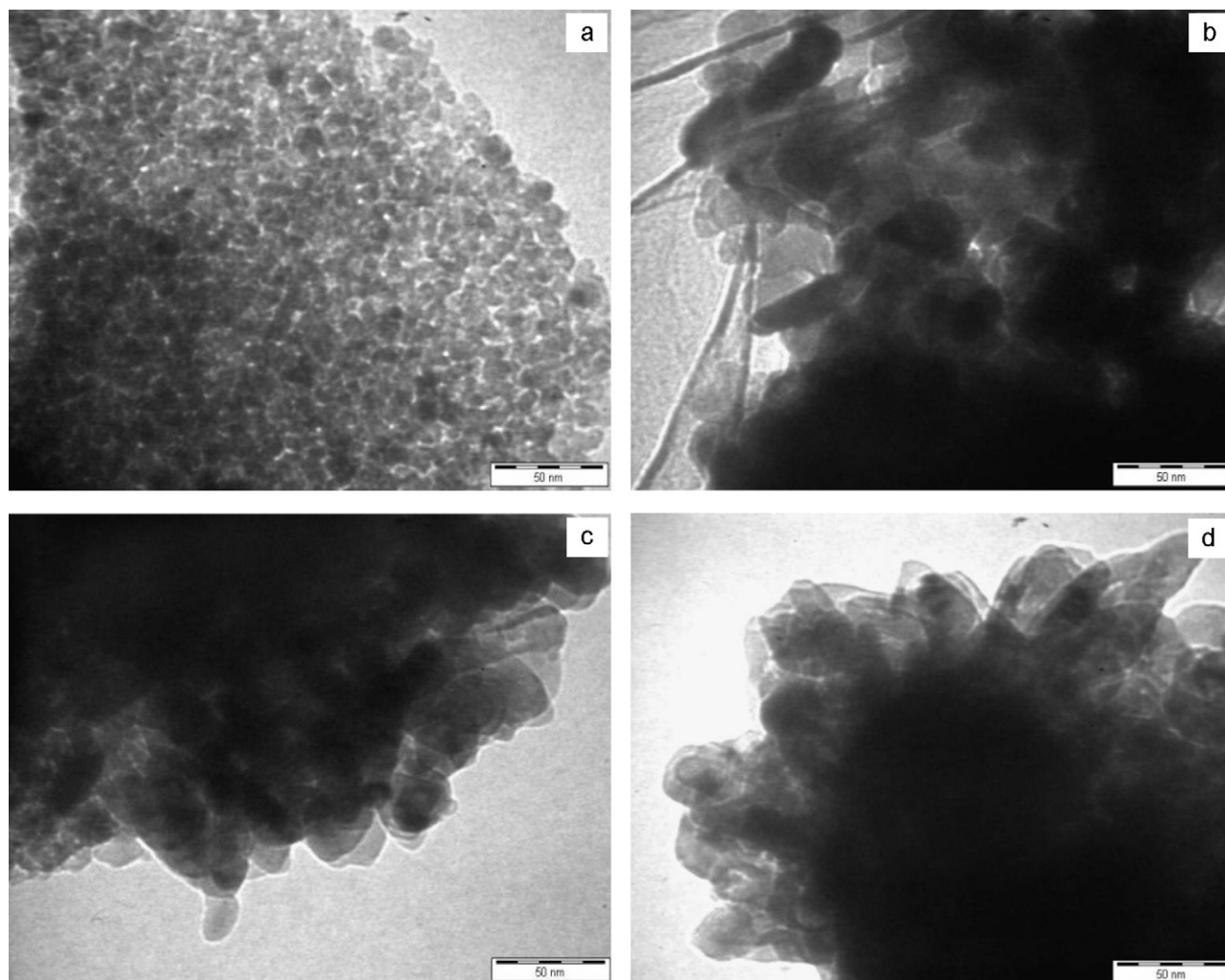


Fig. 2. TEM image of  $\text{TiO}_2$  particles after calcination at  $400^\circ\text{C}$  at different  $\text{H}^+/\text{Ti}^{4+}$  molar ratios: (a) 0.5, (b) 1.5, (c) 2.5 and (d) 3.5.

addition of acid has a strong influence on the crystal structure of  $\text{TiO}_2$ . The XRD pattern of  $\text{TiO}_2$  sol at a 3.5 molar ratio illustrates an anatase phase that has fully transformed into a rutile phase, with dominant XRD peaks at  $2\theta = 27.4^\circ$  and  $54.0^\circ$ . The anatase–rutile phase transformation was accelerated by increasing the acid concentration. This result was confirmed by a TEM image showing nanoparticle of increased size, indicating that phase transformation occurs at an anatase phase with a smaller nanoparticle size rather than in the rutile phase.

Thus, based upon the TEM and XRD observations, the optimal  $\text{H}^+/\text{Ti}^{4+}$  molar ratio was found to be 0.5, with a 2 h peptization process at  $70^\circ\text{C}$ . These conditions were sufficient to yield a blue (semi-opaque) colloidal dispersion as the final product with a predominantly anatase phase.

Table 1  
pH value of  $\text{TiO}_2$  sol at different  $\text{H}^+/\text{Ti}^{4+}$  molar ratios.

$\text{H}^+/\text{Ti}^{4+}$ molar ratio	pH
0.5	1.3
1.5	0.8
2.5	0.4
3.5	0.3

### 3.2. Effect of calcination temperature on $\text{TiO}_2$ membrane

The bond configurations of  $\text{TiO}_2$  membranes calcined at 100, 300 and  $400^\circ\text{C}$  were evaluated by FTIR analysis at wave numbers ranging from 500 to  $4000\text{ cm}^{-1}$  (Fig. 4). For the

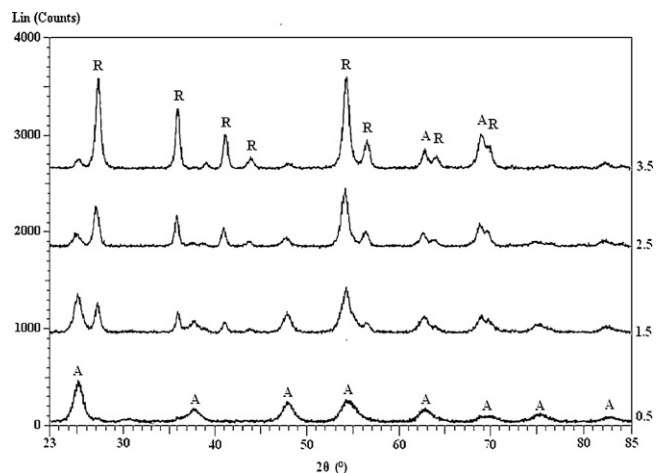


Fig. 3. XRD patterns of  $\text{TiO}_2$  membranes calcined at  $400^\circ\text{C}$  at different  $\text{H}^+/\text{Ti}^{4+}$  molar ratios.



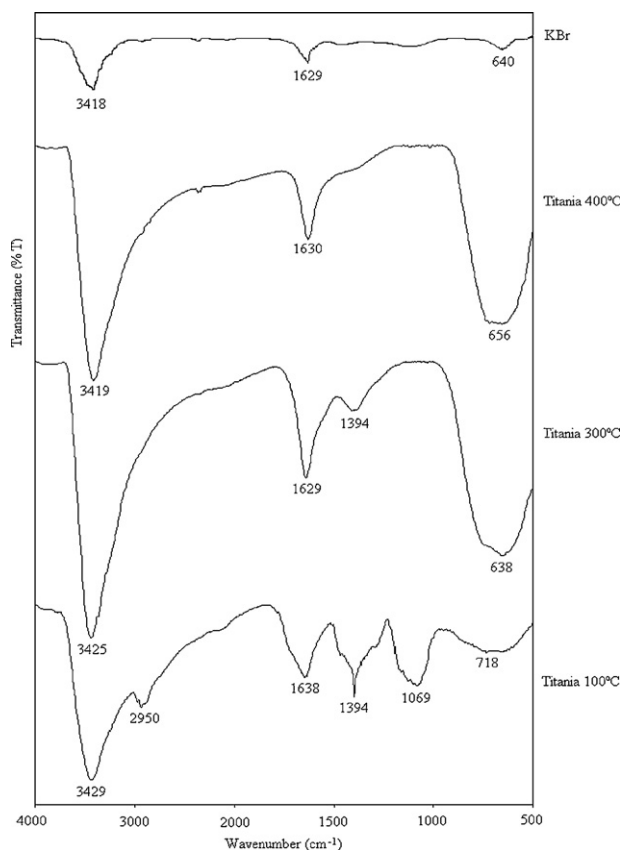


Fig. 4. FTIR spectra of TiO<sub>2</sub> membranes.

membrane calcined at 100 °C, the absorption peak at 3429 cm<sup>-1</sup> indicates the presence of –OH groups, probably belonging to the Ti–OH bonds and the water absorbed by the membrane. The absorption peak of the –OR group of titanium tetraisopropoxide (TTIP), which was the precursor of the TiO<sub>2</sub> sols, appears at approximately 1069 cm<sup>-1</sup>. As the calcination temperature was increased above 300 °C, no absorption peak was detected, implying that the four –OR groups of TTIP were substituted with –OH groups of water. As expected, a full conversion of TTIP was obtained by the hydrolysis reaction, resulting in the formation of TiO<sub>2</sub> particles.

The presence of amorphous TiO<sub>2</sub> was clearly noted by the absorption peak at 718 cm<sup>-1</sup> for the TiO<sub>2</sub> membrane calcined at 100 °C. As the calcination temperature increased, the peak shifted to 638–656 cm<sup>-1</sup>, corresponding to the Ti–O stretching vibration of TiO<sub>2</sub> in the anatase phase. This result is similar to previous reports [20,21].

The absorption peak at 1394 cm<sup>-1</sup> for the TiO<sub>2</sub> membranes calcined at 100 °C and 200 °C corresponds to the nitrate (NO<sub>3</sub>?) group derived from nitric acid. The absorption peak at 2950 cm<sup>-1</sup> for the TiO<sub>2</sub> membrane calcined at 100 °C corresponds to the –CH vibrations associated with the vinyl compounds (–CH=CH<sub>2</sub>) derived from PVA and HPC. All of these features gradually vanished with increasing calcination temperature. This effect was attributed to the oxidation of PVA and HPC due to the heat treatment. The absorption peaks at 3418–3429 cm<sup>-1</sup> and 1629–1638 cm<sup>-1</sup> that appeared for the TiO<sub>2</sub> membranes calcined at 100, 300 and 400 °C indicate the

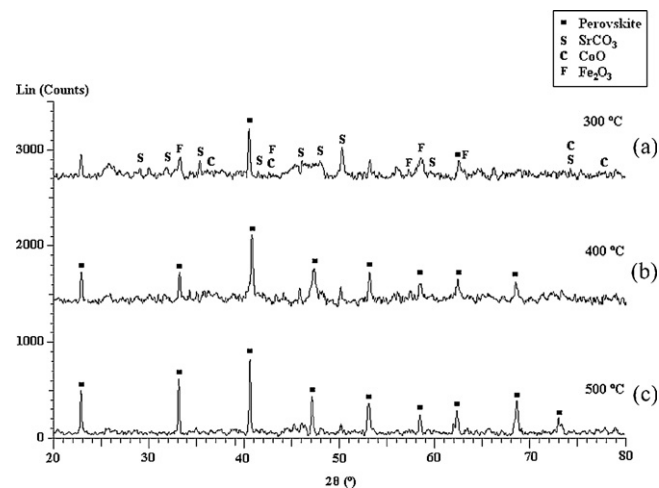


Fig. 5. XRD patterns of SrCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub> calcined at (a) 300, (b) 400 and (c) 500 °C.

presence of –OH groups that belong to the adsorbed water in the KBr pellet.

### 3.3. Effect of calcination temperature on the phase structure of SrCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub>

Fig. 5(a–c) shows the XRD patterns of SrCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub> calcined at 300, 400 and 500 °C, respectively. The SrCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub> calcined at 300 °C (Fig. 5(a)) consists of strontium carbonate (SrCO<sub>3</sub>), iron oxide (Fe<sub>2</sub>O<sub>3</sub>) and cobalt oxide (CoO).

To prepare the SrCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub>, it needed to be calcined until the proper phase was fully achieved. The observations at Fig. 5(a) result from the incomplete oxidation of SrCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub>. Fig. 5(b and c) shows the phase transformation of SrCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub> occurred, as indicated by the dominant XRD peak at 2θ = 40.7°. Based on the experimental results, the SrCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub> structure was readily formed at 400 °C. This finding is consistent with previous reports, where a low temperature perovskite-type CdTiO<sub>3</sub> membrane was prepared [22]. Therefore, 400 °C was chosen as the SrCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub> calcination temperature for the TiO<sub>2</sub> membrane to inhibit the anatase–rutile phase transformation.

### 3.4. Microstructure

An FESEM image of a single coating of a TiO<sub>2</sub> membrane on a membrane support is shown in Fig. 6(a). The TiO<sub>2</sub> membrane was formed on the surface of the support, with some regions remaining uncoated. Cracks were found on the surface of the TiO<sub>2</sub> membrane due to the drying and calcination processes, which removed the water inside the TiO<sub>2</sub> membrane. The release of the water vapor and the shrinkage of the membrane during calcination led to cracks. Fig. 6(b) shows the surface irregularities on the support surface; the thickness of the membrane was estimated to be approximately 0.40 μm. These irregularities are due to the quality of the surface on which the membrane formed. The uneven support surface transfers its roughness to the membrane layers. This roughness is an extra

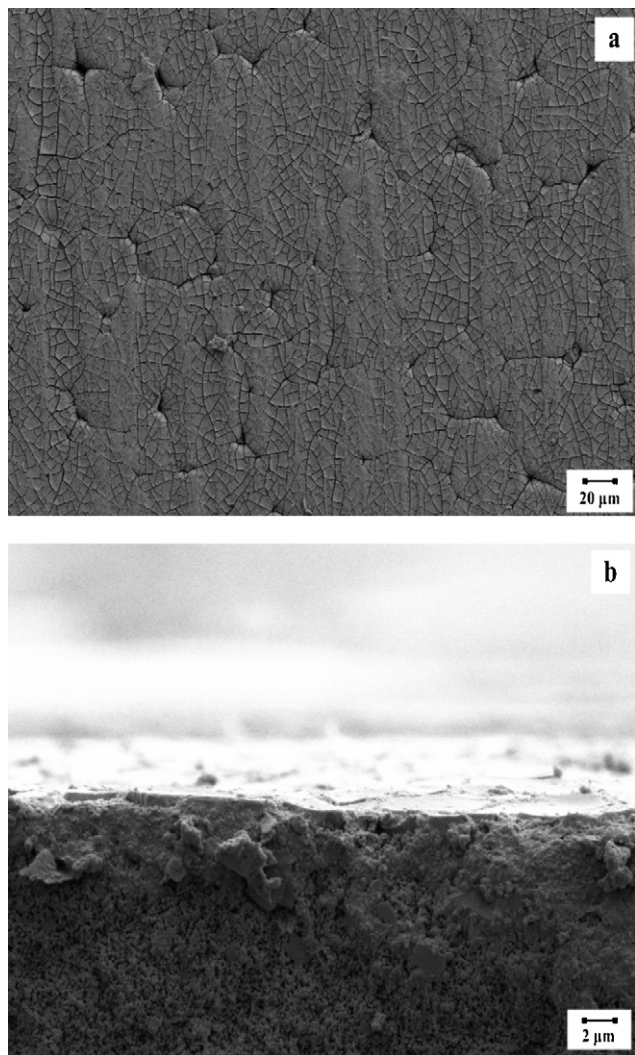


Fig. 6. FESEM images of the  $\text{TiO}_2$  membrane (a) surface and (b) cross-sectional area calcined at  $400^\circ\text{C}$  after a first time dip-coating process.

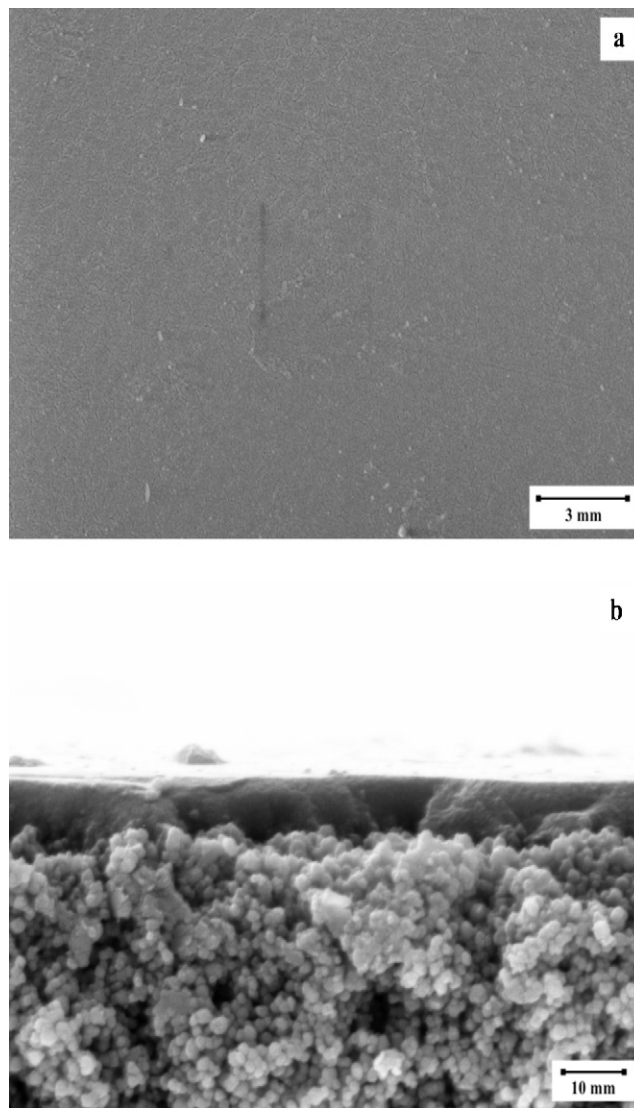


Fig. 7. FESEM images of the  $\text{TiO}_2$  membrane (a) surface and (b) cross-section area calcined at  $400^\circ\text{C}$  after five dip-coating processes.

stress-generating factor that might promote nucleation of cracks and could result in a defective membrane [15].

Fig. 7(a) and (b) shows FESEM images of the surface and cross-section, respectively, of the  $\text{TiO}_2$  membrane after five dip-coating processes. The surface of the  $\text{TiO}_2$  membrane after five coatings became relatively denser and created a more completely coated membrane compared to after a single coating (Fig. 6(a)). Continuous contact exists in the interface, and the thickness of the membrane was found to be approximately  $0.75\ \mu\text{m}$ , as shown in Fig. 7(b). This multiple coating technique can reduce the pore size and coat the entire surface of the porous membrane support. After a crack-free  $\text{TiO}_2$  membrane was obtained, the  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  wet impregnation process was performed.

Fig. 8 shows an image of the  $\text{TiO}_2\text{--SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  membrane, which confirmed the presence of  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  in the  $\text{TiO}_2$  membrane. The surface area of the membrane showed a homogeneous dispersion of  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  particles on the  $\text{TiO}_2$  membrane without cracking.

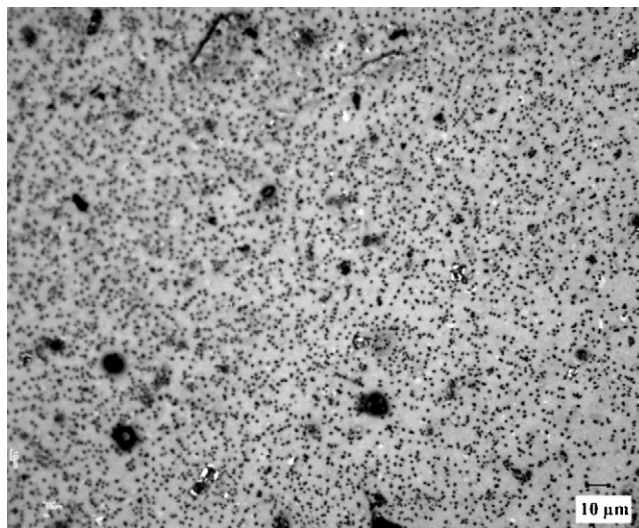


Fig. 8. FESEM image of a  $\text{TiO}_2\text{--SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  membrane calcined at  $400^\circ\text{C}$ .

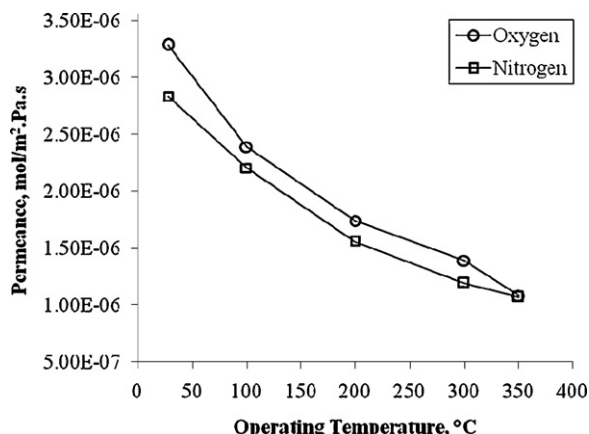


Fig. 9. Permeance of O<sub>2</sub> and N<sub>2</sub> across TiO<sub>2</sub> membrane as a function of the operating temperature.

### 3.5. Gas permeation of TiO<sub>2</sub>–SrCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub> membrane

Although TiO<sub>2</sub> membranes offer numerous applications and advantages, they possess selectivity drawbacks. A TiO<sub>2</sub> membrane not only has a high permeance, but also has a low selectivity. In this work, the selectivity of TiO<sub>2</sub> membranes was improved by doping SrCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub> on the surface of the TiO<sub>2</sub> membrane.

The influence of the operating temperature on the O<sub>2</sub> and N<sub>2</sub> permeances across TiO<sub>2</sub> and TiO<sub>2</sub>–SrCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub> membranes is illustrated in Figs. 9 and 10, respectively. Both figures indicate that as the temperature increased, the O<sub>2</sub> and N<sub>2</sub> permeances decreased. Fig. 9 demonstrates that O<sub>2</sub> exhibited a higher permeance compared to N<sub>2</sub>. However, both the O<sub>2</sub> and N<sub>2</sub> permeances decreased as the operating temperature increased from 28 to 350 °C. As the temperature increased, the permeance of O<sub>2</sub> decreased from 3.29E-06 to 1.08E-06 mol/m<sup>2</sup> Pa s (67.1% drop); the permeance of N<sub>2</sub> decreased from 2.83E-06 to 1.07E-06 mol/m<sup>2</sup> Pa s (62.2% drop). The decreased permeances were mainly due to a gradual reduction in surface diffusion. Generally, the loading factor and surface

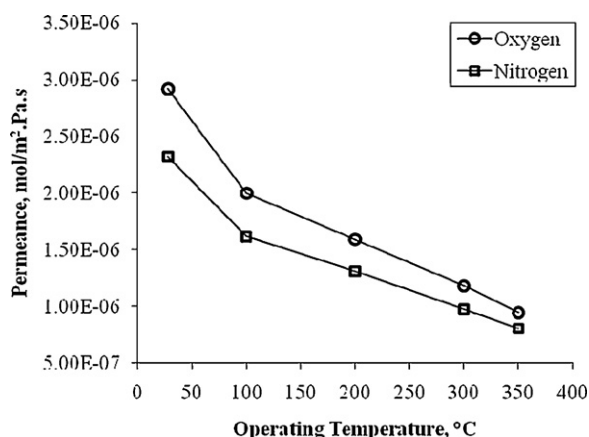


Fig. 10. Permeance of O<sub>2</sub> and N<sub>2</sub> across TiO<sub>2</sub>–SrCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub> membrane as a function of the operating temperature.

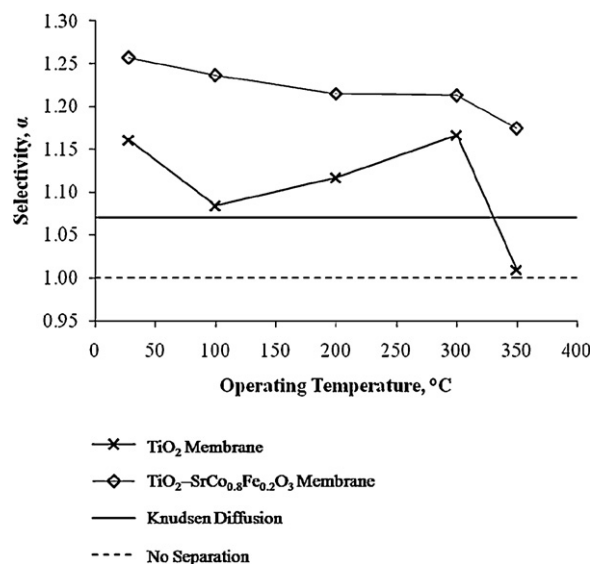


Fig. 11. O<sub>2</sub>/N<sub>2</sub> selectivity of the TiO<sub>2</sub> and TiO<sub>2</sub>–SrCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub> membranes as a function of the operating temperature.

diffusivity will decrease at higher temperatures [23]. This trend is similar to that observed for Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> membranes and indicates that the decrease in O<sub>2</sub> and N<sub>2</sub> permeance as a function of temperature was due to the lower apparent activation energy [24].

The permeation results for the TiO<sub>2</sub>–SrCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub> membrane show a similar trend to the TiO<sub>2</sub> membrane. As seen in Fig. 10, the O<sub>2</sub> permeance decreased from 2.92E-06 to 9.49E-07 mol/m<sup>2</sup> Pa s (a 67.5% drop), while the N<sub>2</sub> permeance dropped from 2.32E-06 to 8.08E-07 mol/m<sup>2</sup> Pa s (a 65.2% drop). The decrease of permeance at higher temperatures was a consequence of improved surface exchange caused by the addition of SrCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub>. The effect on O<sub>2</sub> permeance is more apparent at lower temperatures. The same trend was previously reported using a Ag-doped SrCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3–δ</sub> oxide membrane [25].

The O<sub>2</sub> exhibits a higher permeance, compared to N<sub>2</sub>, for both of the membranes because the order of permeance rates for gases follows the order of kinetic diameters. The kinetic diameter of N<sub>2</sub> (3.64 Å) is larger than that of O<sub>2</sub> (3.46 Å) [26].

Fig. 11 shows O<sub>2</sub>/N<sub>2</sub> selectivity as a function of the operating temperature for TiO<sub>2</sub> and TiO<sub>2</sub>–SrCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub> membranes. It shows that the selectivity for both of the membranes decreased as the operating temperature increased. The TiO<sub>2</sub>–SrCo<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub> membrane shows the highest O<sub>2</sub>/N<sub>2</sub> selectivity (1.26) at 28 °C, while the TiO<sub>2</sub> membrane possesses the lowest O<sub>2</sub>/N<sub>2</sub> selectivity at 350 °C (1.01). The transport mechanism of the O<sub>2</sub>/N<sub>2</sub> selectivity for both membranes predominantly involves the Knudsen diffusion mechanism because the value approaches the theoretical O<sub>2</sub>/N<sub>2</sub> selectivity for the Knudsen diffusion mechanism (1.07), which is defined as the square root of the ratio of the heavier molecular weight gas (O<sub>2</sub>) to the lighter molecular weight gas (N<sub>2</sub>).

The trend for TiO<sub>2</sub> membrane selectivity indicates that the gas permeates mostly through the pores formed in the



crystalline  $\text{TiO}_2$  membrane [27]. The observations indicate that the addition of  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  successfully increased the  $\text{O}_2/\text{N}_2$  selectivity and, at the same time, the ability of the membrane to separate  $\text{O}_2$  from  $\text{N}_2$ . In addition, the increase in  $\text{O}_2/\text{N}_2$  selectivity implies that the large pore size in the  $\text{TiO}_2$  membrane was successfully filled with  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$ .  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  contains several transition metal oxides (Fe and Co) that have been reported to be high-temperature adsorbents for gas separation. In addition, they theoretically have an infinitely high selectivity for  $\text{O}_2$  over  $\text{N}_2$  or other non- $\text{O}_2$  species [28].

#### 4. Conclusion

$\text{TiO}_2$  membranes containing  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  were successfully prepared by the sol–gel method in combination with a wet impregnation process. Based on our findings, the optimal peptization ratio of  $\text{H}^+/\text{Ti}^{4+}$  was found to be 0.5, which results in the formation of a stable and deflocculated sol with  $\text{TiO}_2$  fully in the anatase phase. The optimal calcination temperature for  $\text{TiO}_2$  and  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  was  $400^\circ\text{C}$ . At this temperature,  $\text{TiO}_2$  is fully transformed to the anatase phase, while the PVA and HPC are completely removed, and the oxidation process of  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  is complete. A single coating of the  $\text{TiO}_2$  membrane on the membrane support resulted in cracks and an uneven surface because of the quality of the surface on which the membrane was formed. A crack-free and homogeneous surface of the  $\text{TiO}_2$ – $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  membrane was obtained after multiple dip-coatings of the  $\text{TiO}_2$  membrane, followed by a  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  wet impregnation process. While examining  $\text{TiO}_2$ – $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  membrane performance, it was found that addition of  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  to the  $\text{TiO}_2$  membrane, which acts as a filler phase, successfully increased the  $\text{O}_2/\text{N}_2$  selectivity of the  $\text{TiO}_2$  membrane. The highest selectivity of  $\text{TiO}_2$ – $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  membrane was 1.26, compared to 1.16 for the  $\text{TiO}_2$  membrane. Therefore, it can be concluded that the  $\text{TiO}_2$ – $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3$  membrane prepared using the described method has great potential in applications such as the separation of  $\text{O}_2$  and as an  $\text{O}_2$  enrichment membrane.

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