

Preparation of CaTiO₃ Asymmetric Membranes Using Polyetherimide as Binder Polymer

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ABSTRACT

Asymmetric dense and thin membranes have been prepared from powders of perovskite oxide-type CaTiO₃ without cracking by phase inversion method. Polyetherimide was used as a polymeric binder in the method. The resulting green membranes, composed of CaTiO₃ powder and polyetherimide binder, were sintered at 890, 1100 or 1200 °C. The crystal phase of CaTiO₃ was analyzed using X-Ray Diffraction (XRD). The XRD pattern of the synthesized CaTiO₃ powder was matched with the reference indicating the formation of CaTiO₃ structure. Sintering at 890 °C fails to form a strong membrane. Scanning Electron Microscope (SEM) images of the membranes showed that the membrane had the asymmetric structure with dense layer on one side and porous layer on the other side. The pores in the porous layer were both finger-like and sponge-like structure. The mechanical strength of the membranes, which were determined by Vickers micro hardness method, varied from 3.5 to 25.8 Hv. The strongest membrane without any crack was resulted from sintering at 1200°C with hardness values between 19.4 and 25.8 Hv. Thermal expansion coefficients of the asymmetric membranes sintered at 1100 and 1200 °C, measured with Thermomechanical Analyzer (TMA), were 10.82×10^{-6} and $12.78 \times 10^{-6} \cdot \text{C}^{-1}$ respectively.

Keywords: asymmetric dense membrane; CaTiO₃; perovskite oxide; phase inversion-immersion; solid state method

ABSTRAK

Membran asimetris CaTiO₃ rapat, tipis dan tidak retak telah dibuat dari serbuk oksida perovskit CaTiO₃ dengan metode inversi fasa. Polieterimida digunakan sebagai binder polimer pada metode inversi fasa tersebut. Membran mentah yang merupakan campuran antara serbuk oksida CaTiO₃ dan polieterimida selanjutnya disinter pada suhu 890, 1100 atau 1200 °C. Fasa kristal dari serbuk CaTiO₃ dianalisa menggunakan difraksi sinar-X (XRD). Pola difraksi dari serbuk CaTiO₃ hasil sintesis menunjukkan kesesuaian dengan rujukan yang digunakan yang menunjukkan bahwa CaTiO₃ hasil sintesis memiliki struktur oksida perovskit. Sintering pada suhu 890 °C gagal membentuk membran. Foto Scanning Electron Microscope (SEM) dari membran yang dihasilkan menunjukkan bahwa membran memiliki struktur asimetris dengan lapisan rapat di satu sisi dan berpori di sisi lainnya. Baik struktur pori finger-like maupun sponge-like terlihat pada sisi berpori dari membran. Sifat mekanik membran diuji dengan Micro Vickers Hardness tester dan Thermomechanical Analyzer (TMA). Kekerasan membran, yang diukur dengan micro hardness tester, berkisar antara 3,5 hingga 25,8 Hv. Membran terkeras dan tanpa retak dihasilkan dari sintering pada suhu 1200 °C dengan nilai kekerasan antara 19,4 sampai 25,8 Hv. Koefisien muai panas membran yang disinter pada suhu 1100 dan 1200 °C secara berurutan adalah $10,82 \times 10^{-6}$ dan $12,78 \times 10^{-6} \cdot \text{C}^{-1}$.

Kata Kunci: membran rapat asimetris; CaTiO₃; oksida perovskit; inversi fasa rendam-endap; sintesis padat-padat

INTRODUCTION

During last decades, membrane technology has been widely applied, one of them is to separate the components of mixtures [1]. Inorganic membranes are currently used for the separation of oxygen gas and as the fuel cell material for Solid Oxide Fuel Cells (SOFC). The membranes are semi-permeable to oxygen ions, where the oxygen conduction is a result of reduction and re-oxidation mechanism inside the crystal lattice of membrane materials.

Some membrane materials also have the ability to catalyze the oxidation of hydrocarbons. Therefore, it can be used as a catalyst in producing liquid fuels from natural gas, where the hydrocarbon is mainly non condensable methane, by catalytic oxidative reaction. However, this process requires very strict oxygen control. The oxygen flux in the Partial Oxidation of Methane (POM) can be controlled by using materials that can conduct the oxygen ions. By using this type of membrane materials, the amount of oxygen ion

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supposed to react with the hydrocarbon in natural gas can be controlled to avoid further oxidative reaction [2].

Perovskite oxide is a material that can be used as an oxygen ion conductor and has good catalytic activity for oxidation reactions [3]. The property comes from the fact that the perovskite oxide is able to release the oxygen ion from its crystal lattice without causing significant changes in the structure. The ions are needed to oxidize methane. The releasing of oxygen ions causes the vacancy in the lattice that can be filled again by other ions by reoxidation process [4]. Therefore, perovskite oxide membranes were very selective for oxygen ions transfer. Due to the nature of oxygen transfer in perovskite oxides, free oxygen molecules are not allowed to pass through the holes and/or pores in the membrane. Thus the presences of pores, holes or cracks on the membrane will reduce selectivity of the membrane [5].

Oxygen flux is influenced by several factors: i) the type of perovskite oxides, ii) membrane thickness and iii) surface area. To increase the oxygen flux, it is necessary to reduce the membrane thickness and/or increase the surface area. The thinner the membrane, the higher the oxygen fluxes. However, a thin membrane is very fragile and could be easily cracked and unable to withstand the high temperature and pressure [6]. This problem could be solved by preparing the asymmetric type membrane. This type of membrane consists of a thin but dense layer on top of a thicker porous layer. This would be beneficial because oxygen flux will increase due to the reducing of thickness but, at the same time, strong enough to withstand high temperature and mechanical stress [7].

Asymmetric dense membrane can be prepared by several methods. Recent studies reported that perovskite oxide membrane-type of $\text{La}_{1-y}\text{Fe}_y\text{Co}_{1-x}\text{Sr}_x\text{O}_{3-\delta}$ (LSCF) was made by slurry coating method on raw support [8]. The result is a dense asymmetric membrane and crack free. In this method, a thin membrane composition between dense and porous layers should be appropriate to avoid thermal expansion mismatch. The weakness in this method is time consuming, because of the long stages.

Wei et al. [9] reported the preparation of asymmetric dense membrane of Ytria-stabilized zirconia (YSZ) by phase inversion method. This method used organic polymer membrane as the template for YSZ membrane. The result showed that membrane has an asymmetric structure and production costs could be reduced. Factors to be considered in this method were the type of polymer, solvent, non-solvent, viscosity, sintering temperature, and distribution of perovskite oxide particles.

Yusran [10] conducted a study of preparing asymmetric dense membranes of $\text{LaCo}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ by

using cellulose acetate as a binder polymer. The results show that the membrane is still very brittle and easy to crack although the asymmetric membrane had been densified. However, on the porous layer, pores do not form to the desired structure. The pore has a mixture of sponge-like and finger-like structure. The desired membranes are asymmetric and dense membranes with strong but thin dense layer supported on a finger-like structure of porous layer to induce high oxygen selectivity and flux [11].

Liu et al. [12] reported the preparation of titanium-based membrane, $\text{TiO}_2/\text{Al}_2\text{O}_3$, by phase inversion technique followed by sintering process. The authors use polyetherimide (PEI) as the binder, N-metil-2-pirolidon as the solvent and water as the coagulant. The resulting membranes were asymmetrical with various pores shape and size. Accordingly, PEI was selected in this study as the binder polymer to make CaTiO_3 asymmetrical membranes. PEI polymer is chosen as a binder because it can produce a finger-like pore structure, thus it is expected to form asymmetric dense membrane with finger-like pore structure after sintering. CaTiO_3 was chosen as a model to study the preparation of an asymmetric dense membrane of perovskite oxide.

Sintering is one of the important factors determining the final structure of the desired membranes. According to Tan et al. [13], sintering at temperature above 1400 °C causes excessive densification and resulting in undesired pore structure in its porous layer. Based on the literature, the effect of sintering temperature on the membrane CaTiO_3 is studied in this research.

EXPERIMENTAL SECTION

Materials

The reactants used to prepare perovskite material were technical grade CaCO_3 and TiO_2 (rutile phase). Pro Analyst (p.a) grade of Polyetherimide (PEI) (Sigma Aldrich 98%) was used as polymer binder and N-Metil-2-pyrolidone (NMP) (Merck 99%) was used as a solvent and distilled water was used as non-solvent.

Instrumentation

X-Ray diffraction (XRD) patterns were recorded on Philips XPert MPD. The 2θ scan range was started from 20° to 80°. Surface and cross section morphology of the green bodies and sintered membranes were observed using ZEISS EVO MA 10 Scanning Electron Microscope (SEM). The thermal decomposition of polymer contained in the green body was analyzed

using a Mettler-Toledo DSC-1 Thermogravimetric Analysis under N₂ atmosphere from 25 to 1000 °C with heating rate of 10 °C min⁻¹. Mechanical strength of membranes was measured by micro Vickers Hardness tester. The indentation tests were carried out in the applied force of 5 N and in five points in membrane surface. The diagonal length of each indentation was recorded and averages of diagonal lengths are computed for calculations. The micro hardness value *Hv* was calculated using the formula:

$$Hv = 1.845 \frac{P}{L^2} \quad (1)$$

P is the applied load in N and *L* the diagonal length in micrometers [14]. The membranes were also tested for their thermal expansion coefficient (TEC) using TMA/SDTA METTLER TOLEDO Thermomechanical Analyzer in temperature range 25–1100 °C with heating rate of 25 °C min⁻¹.

Procedure

Synthesis of CaTiO₃ powder

CaTiO₃ powder was used as the membrane materials. The CaTiO₃ perovskite oxide powder was synthesized by solid state method from the powder of CaCO₃ and TiO₂. The reactants were mixed and ground together for 1 h. The mixtures were then calcined at 1200 °C for 4 h. The prepared powders were sieved using 120 mesh sieve to get the fine particle size.

Preparation of asymmetric dense membrane

Asymmetric dense membranes were prepared by phase inversion followed by sintering technique. The detailed preparation procedures were described elsewhere [6]. The NMP was firstly poured to PEI. The mixture was stirred using magnetic stirrer to form a homogeneous paste. The CaTiO₃ perovskite was then added to the paste under stirring. The final mixture was molded into flat shaped green body. The green body was then immersed in a water bath to solidify it. The green bodies were sintered at 890, 1100, or 1200 °C for 4 h each.

RESULT AND DISCUSSION

Crystal Structure of the CaTiO₃

The CaTiO₃ powder was synthesized by the solid state method. Fig. 1 shows XRD pattern of the CaTiO₃ powder. The pattern powder shows pure orthorhombic perovskite phase based on the reference peak taken from PDF No. 00-022-0153. It is proved by the presence of characteristic peaks of CaTiO₃ at 2θ of 33.140, 47.543, 58.888, 59.054, 59.304, 69.454, and 79.173°.

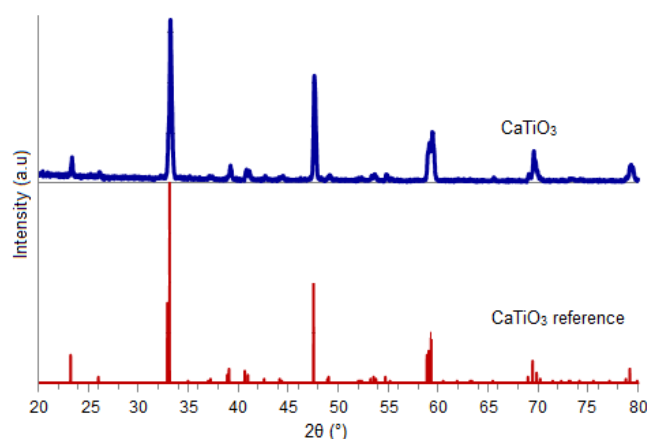


Fig 1. XRD pattern of CaTiO₃ after calcined at 1200 °C for 4 h

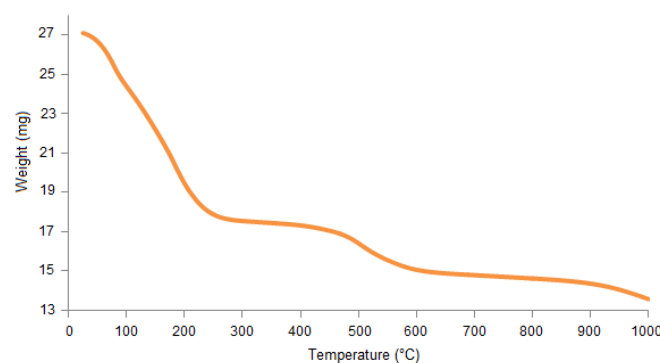


Fig 2. Thermogram DSC-TGA of raw membranes

Asymmetric Membranes of CaTiO₃

Thermogravimetric analysis results shows that PEI was decomposed in some steps as shown in Fig. 2. The decomposition is indicated by the weight lost during the temperature increase. The First mass reduction which is detected at around 100-200 °C corresponds to the releasing of water as vapor that adsorbed on the surface of CaTiO₃ perovskite oxide. The second mass reduction occurs at about 500 °C. It is predicted that the second mass reduction is caused by the decomposition of PEI. The result is consistent with those reported in [15] that PEI was decomposed at 500 °C and the polymer had been removed from the green body. The results indicate that the sintering process can be actually started from this temperature.

The perovskite membrane is used as an oxygen transport membrane. The membrane is able to permeate oxygen via vacancy mechanism where the oxygen ions diffuse along the crystal lattice. This is important to make sure that the membrane is absolutely dense to block other gasses from passing through the membrane [16]. The sintering process is crucial step to make this densification. In this work, the

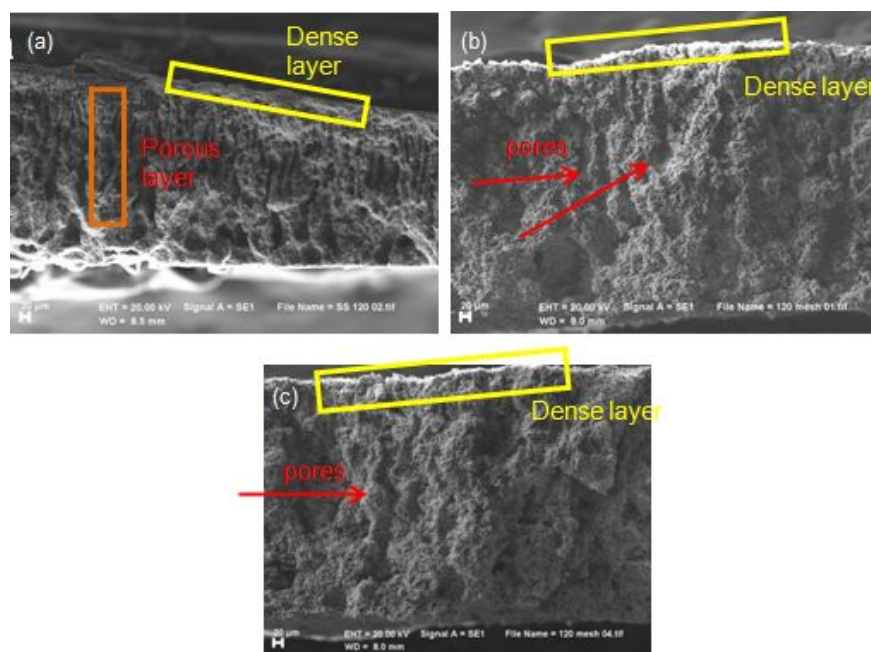


Fig 3. SEM images of membrane cross section: (a) before sintering, (b) sintered at 1100 °C and (c) sintered at 1200 °C

sintering process was carried at 890, 1100 or 1200 °C.

The SEM images of cross section of green body and asymmetric membranes are shown in Fig. 3. Membrane that was sintered at 890 °C is too fragile to be scanned by SEM indicating that the membrane is not sintered very well. The cross section image of the green body and the membranes which were sintered at 1100 and 1200 °C show the presence of a thin and dense layer on the top of an asymmetric structure in both green body and membranes. It implies that the green body could retain its structure after sintering.

Mechanical Strength of CaTiO₃ Asymmetric Dense Membranes

The indentation of asymmetric dense membranes of CaTiO₃ using Vickers hardness instrument with applied force of 5 N reveals that the microhardness value (Hv) of membranes sintered at 1200 °C is higher than membranes sintered at 1100 °C. Hardness of membranes which was sintered at 1100 °C are 3.5 to 21.4 Hv while those sintered at 1200 °C are 19.4 to 25.8 Hv. Higher temperature sintering process leads to higher densification thus the hardness of membranes increase. It implies that the mechanical strength of membrane sintered at 1200 °C is higher than the others.

In addition to hardness, the membranes were also tested for their thermal expansion coefficient (TEC). Different sintering temperature results in different TEC. Membrane that was sintered at 1100 °C has TEC value

of $12.78 \times 10^{-6} \cdot \text{C}^{-1}$ while those sintered at 1200 °C has the value of $10.82 \times 10^{-6} \cdot \text{C}^{-1}$.

CONCLUSION

Asymmetric dense membranes of perovskite oxide-type CaTiO₃ can be prepared by phase inversion method from CaTiO₃ powder using PEI as a binder, followed by a sintering at high temperature without any cracking detected on the resulted membranes. Membrane morphology before and after sintering shows some differences but retain most morphology of their green body. Micro Vickers Hardness test and thermomechanical analysis results show that higher sintering temperature resulting harder membranes and lower thermal expansion coefficient, respectively. Micro hardness value of membranes sintered at 1100 and 1200 °C are 3.5 to 21.4 Hv and 19.4 to 25.8 Hv while their corresponding thermal expansion coefficient are $12.78 \times 10^{-6} \cdot \text{C}^{-1}$ and $10.82 \times 10^{-6} \cdot \text{C}^{-1}$, respectively.

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