Preparation and Characterization of Nanoporous Alumina as Ceramic Membrane Materials

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Abstract. To meet growing electricity demand and greenhouse gas emission limitation in the future, it is urgency to improve existing power plant more efficient and less CO₂ emission. Oxygen combustion instead of air combustion is quite good to raise up the fossil fuels efficiency. And separation oxygen from the air by ionic conductance at high temperatures is promising in large fuel power plants. Ionic separation processes by ceramic dense membrane need a good support porous membranes with good mechanical and permeable property. Present research reports the porous alumina with nanoporous structure was prepared by vacuum filtration and rapid sintering as a kind of porous support layer in the oxygen ceramic separation membrane. The microstructure of nanoporous alumina was analysed, the mechanical properties and gas permeability were tested and compared with some conventional pore-former method made porous ceramics. The uniform nanopores alumina ceramics with both high strength and high permeability achieved by a vacuum filtrate and rapid sintering method is a candidate as the porous support application in fuel cell and gas separation field.

1. Introduction
Global warming is now a serious problem caused by increasing concentration of greenhouse gases in the atmosphere. In order to control the greenhouse effect, carbon dioxide emissions as a major greenhouse gas should be limited.

There are two main aspects to reducing CO₂ emissions without reducing energy supply: firstly it is to improve the combustion efficiency of fossil energy; secondly to improve CO₂ gas adsorption and recovery method. By using oxygen instead of air combustion efficiency enhanced significantly. Therefore, we need for a more efficient method of separating oxygen.

In these decades, a more efficient method to separating oxygen from air have gotten more attention. Practically, pure oxygen is conventionally produced by cryogenic distillation in large scale or by pressure swing adsorption in small scale. But separating oxygen from air at high temperatures in the form of oxygen ionic conductance is more suitable for large fuel power plants by means thermal management.

Although, polymer membranes proved to have promising separation properties at ambient temperature, the chemical instabilities above 100°C is unsolvable. In addition to polymeric membranes, ceramic membranes have been considered, which have a high thermal and chemical stability at high temperature.
Figure 1. Transport processes in dense (left) and porous (right) ceramic membranes.

The key part of this separating plants is an oxygen transport membranes (OTMs) which also called asymmetrical membrane with two part, dense and porous ones. The dense part is gas tight, but have mix ionic electronic conductivity. The oxygen is transported as ions by diffusion inside crystal lattice. So the dense part should have oxygen vacancies. The diffusion process does not need any other energy but the chemical potential between the feed part and the output part. To supply a efficient chemical potential there should be a pressure difference between both sides, Figure 1. In the steady state, oxygen diffusion $j_{O_2}$ through a solid crystal can be described by the Wagner equation:

$$j_{O_2} = \frac{RT}{16F^2} \sigma_{amb} \frac{1}{L} \ln \frac{p'_{O_2}}{p_{O_2}}$$  \hspace{1cm} (1)

where $R$ is the gas constant, $T$ is temperature, $F$ is the Faraday constant, $\sigma_{amb}$ is ambipolar conductivity, $L$ is the membrane thickness, and $p'_{O_2}$ and $p_{O_2}$ are the oxygen partial pressure on the oxygen-rich and oxygen-lean side, respectively.

The only material parameter in the Wagner equation is ambipolar conductivity, which is composed of the ionic $\sigma_i$ and electronic conductivity $\sigma_e$:

$$\sigma_{amb} = \frac{\sigma_e \cdot \sigma_i}{\sigma_e + \sigma_i}$$  \hspace{1cm} (2)

Following the Nernst–Einstein relation, $\sigma_i$ is proportional to the oxygen vacancy concentration $[V_0^\cdot]$, as the vacancy diffusion coefficient $D_V$ can be considered as constant in a certain range of oxygen partial pressures:

$$\sigma_i = \frac{4F^2 [V_0^\cdot]D_V}{RTV_m}$$  \hspace{1cm} (3)

$V_m$ is the molar volume.

To maintain a high oxygen flow it has to increase the operating temperature, reduce the thickness of membrane while raise the pressure between two sides.

A promising possibility is coating of thin membrane layers on top of a porous supports. Due to the high thermal expansion combined with a remarkable chemical expansion, a support from the same composition is favored. The coating and final densification of the membrane layer on top of a sintered support [1]. In last decades several method has been apply to prepare a durable porous supports which possess both good mechanical property and gas permeation.

Porous ceramics can be obtained by mixing appropriate amounts of sacrificial fugitives as pore forming agents with ceramic raw powder and evaporating or burning out them before or during sintering to create pores. J. Malzbender et al. [2] reported a Lanthanum Tungstate substrate for OTM has been prepared by a tape casting method with different porosity varying from 30 to 39% (rice
starch as pore former), ball-on-balls (B3B) biaxial bending strength 66.5-87.4 MPa. This method is apt to applied to industry which is demonstrated by a 150 tons/day pilot plant constructed in 2013 [3]. But the method applied in industry have some limit that the pores formed in the ceramic is uniform sphere. The strength decrease with porosity increase, and the permeation vice versa. Isobe, T. et al. [4] reported porous alumina ceramics with microstructures having unidirectional aligned cylindrical pores with better strength and permeation were prepared by extrusion with fiber as pores former. But the pores and good perform direction are aligned in the extrusion axial direction, which is not apt to membrane.

Zhou, Y. et al. reported SiC tubes, with a porosities of 45.7% to 40.4%, radial crushing strengths of 47 to 110 MPa respectively, made from submicron beta-SiC powder doped with 3 wt% of Al2O3 additive by extrusion and partial sintered [5]. This method is short of adjusting ranges of porosities.

Phase-inversion is generally used for the production of flat, hollow fiber or capillary polymer membranes and is based on the exchange of a solvent and insolvent for the polymer, leading to ‘liquid–liquid’ demixing of the solution and subsequent precipitation of the polymer. C. Buysse et al. [6] developed sulfur-free BSCF capillaries using a sulfur-free phase-inversion polymer. By more attention to both the polymer solution and ceramic suspension they obtain gastight and macrovoid-free BSCF capillaries. Although lack of macrovoids lead to less oxygen fluxes, the overall mechanical strength have been increased and could compromise the gastightness of a sintered membrane or the gastightness during long-term operation by creating weak spots. Moon, Y. W. et al. [7] have developed a manufacturing method combining three-dimensional printing and ceramic/camphene-based coextrusion. They obtain unidirectional macrochannels perpendicular to the membrane and three-dimensionally interconnected pores after removing the camphene. The porosity of the samples is 68% and compressive strength is 28.3 MPa. But this method is too complicated and cost.

In summary the porous ceramic substrate should have both high permeability and high mechanical strength. Whereas the permeation increases with increasing porosity, the strength decrease with increasing porosity, requiring optimization with respect to necessary porosity and microstructure. In this paper bulk porous alumina ceramics with microstructures having uniformly distributed nanopores structure were prepared by a vacuum filtration and rapid sintering method. And the unique performance compared to traditional microporous ceramic materials was studied.

2. Experimental procedure

2.1. Preparation of porous ceramics

As shown in Figure 2, we prepare the nanopores alumina by a vacuum filtration and rapid sintering method. First, a slurry was prepared adding two kinds of α-Al2O3 powder (AKP50, Sumitomo, Japan, SH, Sanhe, China) with mean particle size of 0.2 μm (AKP50) and 0.3 μm (SH) to a 0.02 M dilute nitric acid. The slurry was dispersed for 30 min by an ultrasonic device (5900PR; Panametrics, USA) to form a stable state. Then the excessive dilute nitric acid was removed by a microporous membrane with a vacuum suction filter as seen in Figure 3. The liquid is pumped through the microporous membrane into the conical flask by a vacuum pump for about 2 hours. The colloidal filtered cake formed in vacuum suction, and easy to deform before dried. The colloidal filtered cake was left in the unpermitted side for more than 10 hours to form a solid cake to remove from the vacuum suction. Afterwards, the α-Al2O3 discs were rapid sintered for 1 h at 1000, 1100, 1200, 1300°C in air. After sintering the porous ceramics was grinded to remove deformation part in sintering process to gain a flat shape seen as Figure 4, the round plate with a diameter of about 30mm and 2mm thickness.

2.2. Characterization

Microstructural morphology investigations of porous sample were performed by scanning electron microscopy (SEM; Merlin Compact, Zeiss, Germany) on cross-sections of porous flat sample prepared by cutting and grinding with abrasive papers followed by polishing.

The density and porosity of the sintered samples was measured using Archimedes method (SD200L; Alfa Mirage, Japan). To prevent water from penetrating into the porous alumina sample, a
layer of paraffin is applied to the surface of the sample before the test. When the density is calculated, the weight and volume of the paraffin are subtracted. The flexural strength were tested following ASTM C1161-13, the specimens were cut into 1.5 mm×2mm×25 mm bars and surface polished to mirror to test by 3-point bending (AG-IC; Shimadzu, Japan), with cross-head speed of 0.5 mm/min, and 10 bars were tested for each sample.

The permeability of the porous ceramics was evaluated using Eq. (4):

$$\Delta P = \frac{\eta L}{\mu A} Q$$  (4)

Where P is the pressure drop from entrance to exit of the sample, μ is the Darcy’s permeability, η is the dynamic viscosity of the fluid, A and L are the cross-sectional area and the thickness of the sample, Q is the flow rate. The gas permeability equipment used in this study is shown in Figure 5. The samples cut into 0.5–3 mm in thickness (5 mm Ø in diameter) were fixed in the center of an epoxy resin mold. P and Q were measured using this equipment. The permeability is calculated from the slope of the line plotted for P versus Q using Eq. (1). The dynamic viscosity η of nitrogen gas as used for the calculations $1.75 \times 10^{-5}$ Pa s.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{diagram.png}
\caption{Schematic diagram of material preparation process.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{figure3.png}
\caption{Vacuum suction filter.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{figure4.png}
\caption{Porous Al₂O₃ sample.}
\end{figure}
Figure 5. Schematic model of equipment for gas permeability measurement.

Figure 6. SEM micrograph of 1000°C (a, b) 1100°C (c, d) 1200°C (e) 1300°C (f)sintered cross-sections of porous alumina ceramics prepared by vacuum suction method and AKP sub micrometer powder.
3. Result and discussion

3.1. Microstructure

Figure 6 shows morphology of the porous alumina sample sintered at 1000°C, 1100°C, 1200°C and 1300°C after grind and polish process and wash with ethanol in supersonic device. Since the pores are formed by incomplete sintering between the particles, the connection between the sintered sample particles at 1000°C and 1100°C is weak. A large number of particles are broken at the joints and detached from the porous bulk during the polishing, so the polished sample sintered at 1000°C and 1100°C is still an uneven microstructure. The morphology of the product sintered at 1000°C is relatively loose and uniform porous structure, and the connection between the powder particles is weak. After sintered at 1100°C, the microstructure is still a uniform porous structure, connection stronger and some crushed powder from polishing process trapped in the pores to form some dense parts on the surface, and remained after sonication in ethanol. When the sintering temperature reaches 1200°C and 1300 °C, the porous alumina is obviously densified, and the uniform porous structure transformed into partially dense product, remained some irregular shape uneven distribution pores.

Figure 7 shows the morphology of porous alumina sample sintered at 1100°C surface treated by ionic milling. Argon ions hitting the surface of the sample at high speed keep particle without rapture from the joint which keep the polishing cross-section flat to get a clear appearance of porous structure. In low magnification image, it shows that the sample has quite a uniform structure. In high magnification image, it shows the powder particle partially sintered to form a neck junction. Leaving narrow pores with a width of tens of nanometers between particles.

Figure 7. SEM micrograph of cross-sections of porous alumina ceramics by AKP50 powder after ionic milling.

By comparing the microscopic morphology of porous alumina samples sintered at different temperatures, we found that the temperature has a significant effect on the grain bonding and pore morphology of the vacuum filtration powder cake. When the temperature is sintered at a lower temperature, weak joints are formed between the crystal grains, and uniform pores left between the alumina grains. When the temperature is sintered at a higher temperature, the crystal grains are further sintered, and the local crystal grains are completely densified, leaving pores with uneven distribution.

To compare the effects of powders sizes and morphologies on the microstructure and porosity of the products, we used the same method to prepare porous alumina bulk with domestic SH powder. The mean particle size of the powder is 0.3 micron, slightly higher than AKP50. During the vacuum filtration process, we found that the slurry prepared by SH powder was quickly extracted out of the suction filter, the powder cake was formed within 1 minute, but the strength of the powder cake was worse than of AKP50. The cross section of the product was treated by the same cutting, polishing and ion milling methods. The morphology of the product showed that the porous alumina prepared by SH powder had a non-uniform pore size distribution. Through rapid sintering, a neck joint was formed...
between some grains, but not all grains packed densely, forming agglomeration and leaving a large number of large pores. Therefore, the particle size distribution, shape and other factors affecting the powder packing characteristics have an important influence on the micro-morphology of the porous material prepared by the vacuum suction filtration and rapid sintering methods.

![SEM micrograph of cross-sections of porous alumina ceramics by SH powder.](image1)

**Figure 8.** SEM micrograph of cross-sections of porous alumina ceramics by SH powder.

![Porosity and sintering temperature of porous ceramics.](image2)

**Figure 9.** Porosity and sintering temperature of porous ceramics.

### 3.2. Porosity, mechanical properties and permeability

It can be seen from Figure 9 that with the increase of the sintering temperature of the green body prepared by vacuum filtration of AKP powder, the porosity of the product decreases rapidly. When the sintering temperature reaches 1200 °C, the product changes from a porous bulk to a nearly dense structure, which consist with the results of the SEM microstructure. In addition, the porosity of the powder cake prepared by vacuum filtration using SH powder is relatively high, and the changes with the sintering temperature not significant. According to the result of the morphology of the product, AKP powder compact cake obtained by the vacuum filtration method can obtain a uniform nanoporous structure by rapid sintering at 1000°C and 1100°C. The nanoporous structure will further densified at a higher temperature, and destroy the porous structure, and the densification of the non-compacted powder cake is not remarkable.
Figure 10 shows the relationship between the three-point bending strength and the material porosity. For a porous support material, it requires a higher porosity to maintain better gas permeability and also requires better mechanical strength to provide support. Porous alumina prepared by vacuum filtration using AKP powder as a raw material has a flexural strength of 148.18 MPa when the porosity is 29.23%, and a bending strength of 115.30 MPa when the porosity is 35.13%. In addition, the porous alumina prepared by using SH powder as a raw material has a porosity of 50% to 60%, and the bending strength does not change much, and is about 25 to 30 MPa. For comparison, here we listed the relationship between the porosity and flexural strength of porous materials prepared by the conventional pore former method in the literature, and the materials listed are all applied as support layers in the oxygen separation membrane. The circled area contains the porosity and bending strength relationship of the porous material prepared by the conventional method. It can be seen that the porous material prepared by the vacuum suction filtration and the rapid sintering method has higher bending strength at a similar porosity than the conventional method.

Figure 10. Relationships between flexural strength and porosity of porous ceramics.

Figure 11. Relationships between gas permeability and porosity of porous ceramics.
In the past, the discussion on the relationship between the strength of porous materials and the porosity was mostly applied to the conventional porous material prepared by pore former method or foam method, the model was not applicable to the nanopores structure described herein. Zhang\textsuperscript{8} believes that the nanopores structure is much smaller than the structure of the conventional method, and there are more contact points in unit volume between the crystal grains, and the pores induce crack propagation and absorb the crack propagation energy, so more nanometer small pores can cause more crack deflection points to increase material strength.

Finally, we tested the gas permeability of porous alumina, and the results are shown in Figure 11. The permeability of the samples is $1.60 \times 10^{-14} \text{ m}^2$ at 35.13\% porosity and $2.25 \times 10^{-16}\text{ m}^2$ at 29.23\% porosity which is higher than the conventional samples. Better gas permeability here maybe due to more effective permeable structure as the flow of liquid during the filtration process.

4. Conclusions

Bulk porous alumina ceramics with microstructures having uniformly distributed nanopores structure were prepared by a vacuum filtration and rapid sintering method. The mechanical and gas permeability properties were investigated after. After ionic milling surface treatment the SEM micrographs of the $900^\circ\text{C}$ porous alumina ceramics prepared by the vacuum filtration and rapid sintering at 1100\textdegree\text{C} for 1 hour showed uniform neck joints formed between submicron powder particles and pores of 50-200nm left in the gap of the powders. Powder neck joints, pores structure and porosity changed with sintering temperature, the neck joints became a dense connection between multiple powders, and the pores exist in an irregular shape between the dense powders. The shape of the powder also have an important influence on the morphology of the pores and the uniformity of particles. The characteristics of the powder and the temperature of the sintering have an important influence on the porosity of the porous alumina, the porosity sintered at 1000\textdegree\text{C} and 1100\textdegree\text{C} AKP-50 powder is 29.23\% and 35.13\%. The strength of the porous samples was 148.18 MPa at 29.23\% porosity and 56.03MPa at 35.13\% porosity higher than the conventional ceramics due to smaller pores can then lead to more crack deflection sites and hence energy absorption. The permeability of the samples having $1.60 \times 10^{-14} \text{ m}^2$ at 35.13\% porosity and $2.25 \times 10^{-16}\text{ m}^2$ at 29.23\% porosity is higher than the conventional samples which may due to a more efficient pore penetration structure. The uniform nanopores alumina ceramics having both high strength and high permeability are achieved by a vacuum filtration and rapid sintering method which is a candidate as the porous support application in fuel cell and gas separation field.

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