

# Effect of Type and Content of Pore-forming Agents on Properties of Porous Alumina Membrane Support

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**Abstract.** Porous ceramic membrane support with high porosity and high mechanical strength has been fabricated by adding the pore-forming agents, and using three particle sizes of alumina (coarse, medium and fine) as raw material. The effects of the type and the content of the pore-forming agents on the porosity, pore diameter and flexural strength of the membrane supports are studied in detailed. The results show that both the type and the content of the pore-forming agent can be effectively optimized to improve the mechanical and microstructural properties of the alumina support. Added 5 wt% of starch as the pore-forming agent, the porous ceramic membrane support calcinated at 1650°C for 2 h has the porosity of >33%, the flexural strength of > 45 MPa, the pore size of about 6~8  $\mu\text{m}$ . The amount of pore-forming agent plays a decisive role on the porosity and pore size of porous ceramic membrane support based on SEM characterization.

## 1. Introduction

Membrane separation technology have the advantages of high efficiency, low energy consumption and environmental friendliness, which becomes a key development technology for various applications [1-2]. Among various membranes, ceramic membranes have drawn significant interests, due to their resistance to high temperature, acid, alkali and corrosion, and many high performances such as the high mechanical strength, the washing recyclability, the long lifetime and so on. As a result, they have been widely used in petrochemical, chemical, pharmaceutical, food and other industries [3-4]. Generally, Ceramic membranes have the asymmetric structure, i.e. and the separation layer or the transition layer is prepared on the porous support which provides them with sufficiently large interface and mechanical strength [5]. Therefore, the porous support is a key component of porous ceramic membranes.

Generally, the porous support is required to have a high porosity ( $\geq 30\%$ ) with a sharp pore size distribution and a high flexural strength ( $\geq 40\text{MPa}$ ). The pore-forming agent is generally used to prepare the porous support, which is verified by the theory and the practice. The pores are easily formed by the original position of the pore forming agent after the pore-forming agent being oxidized and removed during the sintering process [7-9]. Carbon-based materials are often used as pore-forming agent, such as carbon powder, fiber, wood chips and starch [10-11]. For example, Yao et al [12] prepared hydroxyapatite composite ceramics using polymethacrylate as the pore-forming agent to control the pore diameter.

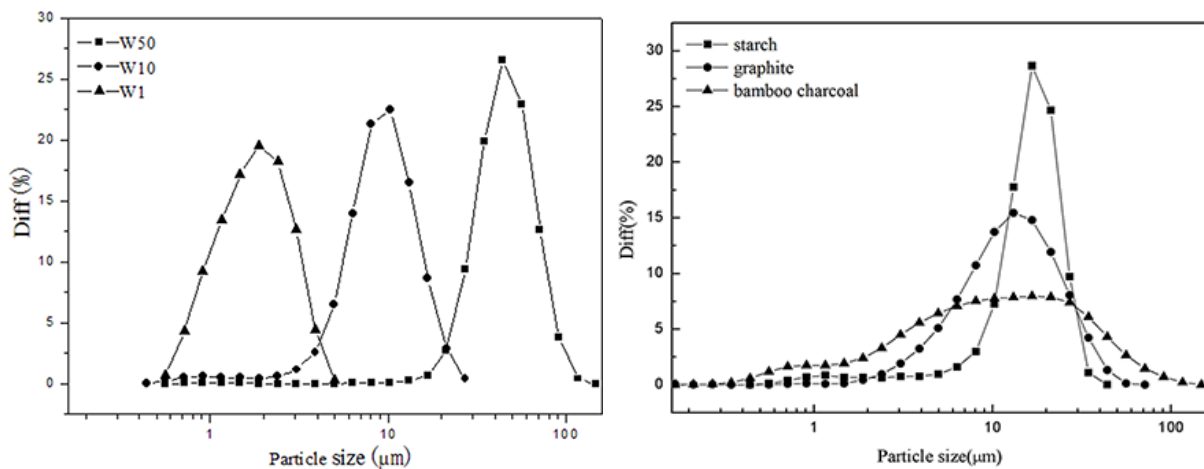
Obviously, the species and the content of the pore-forming agent play a significant role in fabricating



porous support with the given porosity and mechanical properties, and then the size of the pores is decided by the size of the pore-forming agent. In the present work, three particle sizes of alumina (coarse, medium and fine particles) were selected as the raw materials to fabricate the porous supports by adding starch, graphite and bamboo charcoal as the pore-forming agent. Specifically, the effects of the types and contents of the pore-forming agents on the porosity are systematically studied, as well as the mean pore size and the flexural strength of the porous support.

## 2. Experimental

### 2.1. Preparation of ceramic membrane supports



**Figure 1.** Particle size distribution of the raw materials

Alumina ( $\alpha$ - $\text{Al}_2\text{O}_3$ , purity  $\geq 99\%$ ) powders (Luoyang, Henan Province, China) were purchased and used as the raw materials without further treatment. The particle size distribution of the three alumina powders and the three pore-forming agents (starch, graphite and bamboo charcoal) are shown in Fig.1, respectively. The median sizes ( $d_{50}$ ) of the three alumina powders (coarse, medium and fine particles) are  $37\text{ }\mu\text{m}$ ,  $8.2\text{ }\mu\text{m}$  and  $1.6\text{ }\mu\text{m}$ , respectively, which are denoted as W50, W10 and W1. The compaction density of starch, graphite and bamboo charcoal are  $0.53\text{g/cm}^3$ ,  $0.56\text{g/cm}^3$  and  $0.64\text{g/cm}^3$ . 2wt%  $\text{TiO}_2$  was used the sintering aid.

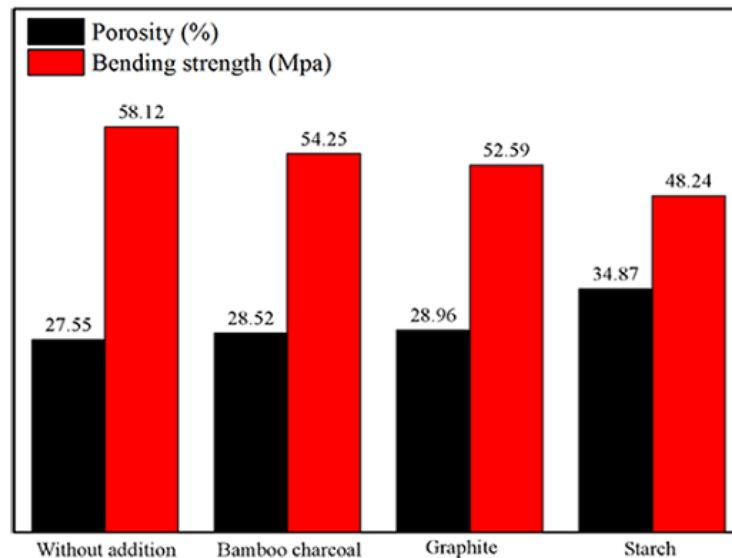
The W50, W10 and W1 alumina powders were mixed with a ball mill at 150rpm for 2h at the weight ratio of 7:2.4:0.6. Starch, graphite or bamboo charcoal was added, together with 2%  $\text{TiO}_2$  into the mixed alumina powders. In the ball mill, the mass ratio of powder: alumina ball: alcohol is 1:1:1.8. The obtained suspensions were dried in an oven at  $65^\circ\text{C}$  for overnight. The dried mixed powders were pressed into the bar with a dimension of  $30\text{mm}\times 9\text{mm}\times 5\text{ mm}$  ( $L\times h\times w$ ) by dry pressing (12MPa). They were finally sintered at  $1650^\circ\text{C}$  for 2 h.

### 2.2. Characterization

Morphology and microstructure of the samples were observed by FE-SEM (JSM-6700F, Japan). Particle size distribution of the powders was measured by a laser particle size analyzer (Bettersize2000, Dandong, China). The bending strength of the samples was tested by using computer controlled material testing machine (WSD-10kN, Xi'an Lichuang, and China). Pore diameter distribution and the porosity of ceramic membrane supports were tested by an Auto pore (IV9500, Micromeritics).

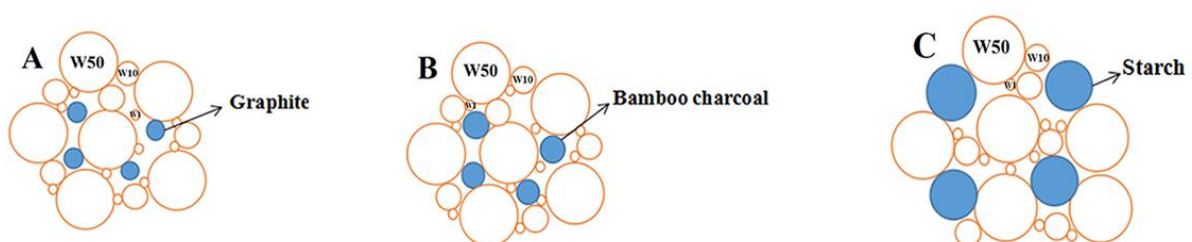
### 3. Results and Discussion

#### 3.1. Relationship of the type of pore-forming agent with properties of supports



**Figure 2.** Bending strength and the porosity of supports with 5% Bamboo charcoal、Graphite or Starch

The porosity of the sintered supports depends on the distribution of alumina with pore-forming agent. Fig.2 shows the bending strength and porosity of supports with 5% bamboo charcoal, graphite or starch. As can be seen, the porosity of ceramic membrane support increase effectively due to the addition of the pore-forming agents. Unfortunately, the flexural strength is also decreased. However, the ratio of the increase in porosity is higher than that of the decrease in flexural strength. As compared with the support without the use of pore-forming agent, the starch-support has an increase in porosity by 26.57% and a decrease in flexural strength by 16.99%. In comparison, the addition of graphite and bamboo charcoal result in the increase in porosity of only 5.12% and 3.52%, respectively.



**Figure 3.** The mixed state of alumina with pore-forming agent by pressure

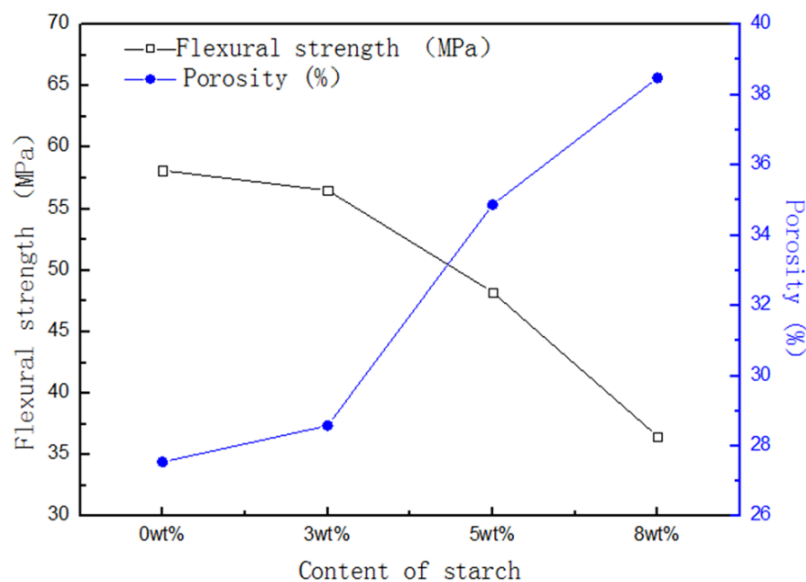
Fig.3 shows the mixed state of alumina with pore-forming agent by pressure. As can be seen, the bamboo charcoal and graphite particles are full of the gap formed by alumina powders, due to the rearranged of powders. Then the green density of support with addition of bamboo charcoal and graphite is higher. Thus, the pore-forming agent was carbonization and the shrink of support by sintered, so the porosity of support has little change. However, when the starch as the pore-forming agent, due to the starch has bigger particles size with narrower particle size distribution, the starch mixes uniformly with alumina powder and locates among the coarse alumina particles. Starch occupies the position of alumina, as shown in Figure 3-C. During the sintering process, after the starch being volatile and oxidized, the uniform space is produced. It contributes to the increase of the porosity [13-14].

However, the mechanical properties of porous support have been experimentally formularized as a function of porosity, which is quoted in. [15] accordingly, the empirical relationship is given by the following equation:

$$\sigma = \sigma_0 \exp(-\beta \varepsilon) \quad (1)$$

Where  $\sigma$  and  $\sigma_0$  are the strengths of the porous support and without pores, respectively.  $\beta$  Is the parameter determined by the nature of porosity, and  $\varepsilon$  is the porosity. According to Eq (1), the strength of porous support decreases exponentially with increasing the porosity. Therefore, when adding the same content and different types of pore-forming agent, the porosity of support depends on the particles size distribution of the pore-forming agent, and the bending strength decreased with increasing the porosity.

### 3.2. Relationship of the content of starch with porosity and bending strength of supports

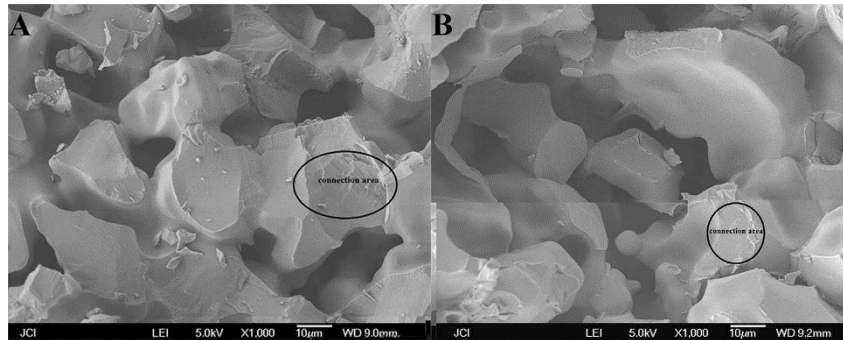


**Figure 4.** Bending strength and the porosity of the supports with different contents of starch

Fig.4 shows the bending strength and the porosity of the porous ceramic membrane supports which have the function of the different content of starch. When the content of starch is 3wt%, the bending strength of the porous ceramic membrane support decreases by 2.77%, and the porosity increases by 3.74%, compared with the sample without the use of pore-forming agent. If the content of pore-forming agent increases from 3wt% to 5wt%, the bending strength reduces by 14.63% and the porosity increases by 22.01%. However, the content of starch increases further to 8wt%, which results in the sharp decreasing by 24.32%, however, the porosity increases only by 10.35%. In other words, over high level of pore-forming agent results in the sharp decrease in the bending strength of the membrane supports, whereas the contribution of porosity is less pronounced.

The above experimental results can be explained as follows. When the content of starch is less than 3 wt% (the compaction volume of starch is  $5.66\text{cm}^3$ ), the starch particles mainly locate at the spaces formed by the aggregation of the alumina granules. Moreover, the spaces cannot be completely filled with the starch particles. As a consequence, there is no properties difference between the porous ceramic membrane support with 3wt% starch added and that without starch added. When the content of starch increases from 3wt% to 5wt% (the compaction volume of starch is  $9.44\text{cm}^3$ ), as the discussed above, the starch particles can full of almost in all the space among the aggregated alumina granules, while the

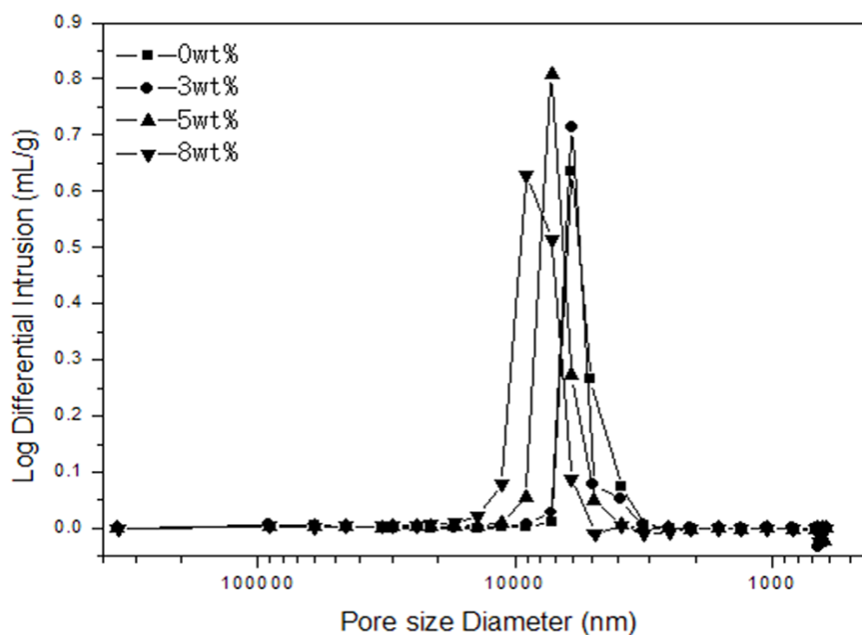
excess starch can also occupies the position of alumina as the coarse particles. With increasing the content of starch, the volume of the pore-forming agent is increased. Therefore, the starch occupies the more position of alumina, and the porosity of supports is further increased by sintered.



**Figure 5.** Cross-sectional SEM images of the supports with different contents of pore-forming agent: (A) 0 wt% and (B) 8 wt%

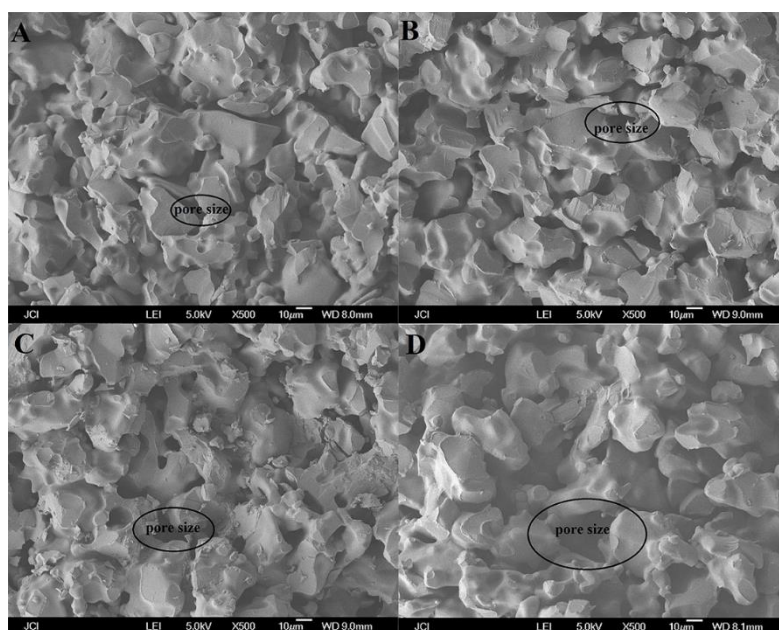
As for porous ceramic, the bending strength of supports depends on the connection area among the grains in support's framework. Fig.5 shows the bending strength decreases with the increase of the content of starch. The reason is that a large amount of starch occupies the position of alumina particles, Increased the porosity results in reduces the connection area between the alumina particles by sintered. Compared with the support without starch added, as the content of starch be added to 8wt% (the compaction volume of starch is  $15.09\text{cm}^3$ ), the distribution of the starch particles is continuous, and the alumina grains are separated completely. As shown in Figure 6, the connection area of alumina particles decrease, which results in the sharp drop in the bending strength. Similar trend has been reported in the open literature [16].

### 3.3. Relationship of the content of starch with pore size distribution of supports



**Figure 6.** Pore size distribution of the supports with different contents of starch

The pore size distribution of the support with different content of starch is shown in Fig.6, It can be seen that the mean pore size increases gradually with the increasing of starch content. At the same time, the pore size distribution changes slightly wider. It can be explained that wwhen the content of starch increases from 3wt% to 5wt%, and the starch occupies the less position of alumina and increase the pore size. However, the pore size distribution have less changes. If the starch content increases further to 8wt%, the amount of starch leads to the continuous phase formed by starch. At the same time, the starch particles together with each other to forms large particles filled between alumina particles. After sintering, the large gap formed by starch results in the larger pore size of the porous ceramic membrane support. Yang [17] had observed that the addition of starch would increase the pore size. So with increasing the content of pore-forming agents, the mean pore size increases and the pore size distribution of support changes wider.



**Figure 7.** Cross-sectional SEM images of the porous supports with different contents of pore-forming agent: (A) 0 wt%, (B) 3 wt%, (C) 5 wt% and (D) 8 wt%

Fig.7 shows cross-sectional SEM images of the porous membrane supports with different contents of starch. As can be seen, the mean pore size increases gradually with the increase content of starch added.

#### 4. Conclusion

The pore-forming agent method has been used to increase the porosity of the porous ceramic membrane supports. Both the type and the content of the pore-forming agent are effectively optimized to improve the mechanical and the microstructural properties of the alumina support. When adding the same content and different types of pore-forming agent, the porosity of support depend on the particles size distribution of pore-forming agent. In our present study, with the increase of the starch content, the mean pore size and the porosity increases gradually and the permeability of the supports also increases. However, the addition of more content of starch( $\geq 8\text{wt}\%$ )will cause a sharp decrease in the bending strength of support, which is harmful to the performance of the support.

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## References

- [1] X. Y. Li, Y.Q. Wang, J.F. Pan, Z.J. Yang, Y.B. He, A.N. Mondal, T.W. Xu, The preparation and application of a low-cost multi-channel tubular inorganic–organic composite microfiltration membrane, *Sep. Purif. Technol.* 151 (2015) 131 - 138.
- [2] P. S. Goh, A. F. Ismail, A review on inorganic membranes for desalination and wastewater treatment, *Desalination*. 434 (2018) 60 - 80.
- [3] Y. L. Yang, J.E. Zhou, Q.B. Chang, K. Yang, Y.Q. Wang, Effects of nano-TiO<sub>2</sub> on the sintering process of aluminum oxide porous ceramic membrane support, *J. Synth. Cryst.* (in Chinese). 44 (2015) 2841 - 2846.
- [4] S. Sarkar, Process for preparation of low cost clay-alumina multichannel ceramic membrane for liquid filtration application, *Trans. Indian. Ceram. Soc.* 73 (2014) 239 - 244.
- [5] Q. B. Chang, Y.L. Yang, X.Z. Zhang, Y.Q. Wang, J.E. Zhou, X. Wang, S. Cerneaux, Y.C. Dong, Effect of particle size distribution of raw powders on pore size distribution and bending strength of Al<sub>2</sub>O<sub>3</sub> microfiltration membrane supports, *J. Eur. Ceram. Soc.* 34 (2014) 3819 - 3825.
- [6] G. Pia, L. Casnedi, U. Sanna, Porous ceramic materials by pore-forming agent method: an intermingled fractal units analysis and procedure to predict thermal conductivity, *Ceram. Int.* 41 (2015) 6350 - 6357.
- [7] N. Obradović, S. Filipović, S. Marković, M. Mitrić, J. Rusmirović, A. Marinković, Influence of different pore-forming agents on wollastonite microstructures and adsorption capacities, *Ceram. Int.* 43 (2016) 7461 - 7468.
- [8] J. F. Yang, G.J. Zhang, T. Ohji, Fabrication of low - shrinkage, porous silicon nitride ceramics by addition of a small amount of carbon, *J. Am. Ceram. Soc.* 84 (2010) 1639 - 1641.
- [9] N. Obradović, S. Filipović, J. Rusmirović, G. Postole, A. Marinković, D. Radić, Formation of porous wollastonite-based ceramics after sintering with yeast as the pore-forming agent, *Sci. Sinter.* 49 (2018) 235 - 246.
- [10] S. Sarkar, S. Bandyopadhyay, A. Larbot, S. Cerneaux, New clay–alumina porous capillary supports for filtration application, *J. Membr. Sci.* 392 (2012) 130 - 136.
- [11] R. Khattab, A. El-Rafei, M. Zawrah, Fabrication of porous TiO<sub>2</sub> ceramics using corn starch and graphite as pore forming agents, *Int. Int. Ceram. R.* 67 (2018) 30 - 35.
- [12] X.M. Yao, S.H. Tan, D.L. Jiang, Improving the properties of porous hydroxyapatite ceramics by fabricating methods, *J. Mater. Sci.* 40 (2005) 4939 - 4942.
- [13] Z. Živcová-Vlčková, J. Locs, M. Keuper, Microstructural comparison of porous oxide ceramics from the system Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub>, prepared with starch as a pore-forming agent, *J. Eur. Ceram. Soc.* 32 (2012) 2163 - 2172.
- [14] J. J. Liu, Y.B. Li, Y.W. Li, S.B. Sang, S.J. Li, Effects of pore structure on thermal conductivity and strength of alumina porous ceramics using carbon black as pore-forming agent, *Ceram Int.* 42 (2016) 8221 - 8228.
- [15] Y. Hirata, T. Shimonosono, T. Sameshima & S. Sameshima, Compressive mechanical properties of porous alumina powder compacts, *Ceram. Int.* 40 (2014) 2315 - 2322.
- [16] X. J. Ding, J.Z. Zhang, Research on the porous supporting body of alumina, *Membr. Sci. Technol.* 20 (2000) 17 - 21.
- [17] G. C.C. Yang, C.M. Tsai, Effects of starch addition on characteristics of tubular porous ceramic membrane substrates, *Desalination*. 233 (2008) 129 - 136.