applied sciences

MDPI

Article

Preparation of a High-Performance Porous Ceramic Membrane by a Two-Step Coating Method and One-Step Sintering

Zhiwen Hu [1], Yulong Yang [1,*], Qibing Chang [1], Fengli Liu [1], Yongqing Wang [1] and Jinfeng Rao [2]

[1] School of Materials Science and Engineering, Jingdezhen Ceramic Institute, Jingdezhen 333403, China; huzhiwen@jci.edu.cn (Z.H.); changqibing@jci.edu.cn (Q.C.); liufengli@jci.edu.cn (F.L.); wangyongqing@jci.edu.cn (Y.W.)

[2] Civil Engineering and Urban Construction College, Jiujiang University, Jiujiang 332005, China; Isabelrao520@163.com

* Correspondence: yyl0822@126.com; Tel.: +86-798-8461173

Received: 17 November 2018; Accepted: 19 December 2018; Published: 24 December 2018

Abstract: Hole defects and uneven membrane thicknesses can lead to poor performance, especially in the separation stability of ceramic membranes. This paper uses a one-step sintering method, which avoids hole defects and uneven membrane thicknesses, for the preparation of high-performance and defect-free ceramic membranes. For this purpose, two kinds of ceramic membrane slurry with high or low viscosities were prepared by alumina particles, as raw materials. Both the effects of the two coating process with a one-step coating method for low-viscosity slurry, and the two-step coating method with a high viscosity flush after a low viscosity coating, on the surface properties of a ceramic membrane, were studied in detail. The result shows that the properties of ceramic membranes can be improved by a two-step coating method, with a high viscosity flush after a low viscosity coating, A high-performance and defect-free ceramic membrane was obtained by one-step sintering at 1450 °C for 2 hr with 7 wt % solid content and a coating time of 11 s.

Keywords: ceramic membrane; preparation process; two-step coating method; one-step sintering; high-performance

1. Introduction

Porous ceramic membranes have been widely used in the fields of gas and liquid filtration, purification, separation, thermal insulation, and other applications, and they have the advantages of high porosity, high temperature resistance, good corrosion resistance, and high chemical stability [1–4]. A ceramic separation membrane can be seen as a kind of gradient porous ceramic material, which generally consists of a transition layer and a thin separation layer with a porous support requiring two-step sintering. The support is required to provide high mechanical strength and flow in transporting the thin separation-layer membrane [5–7]. However, the separation layer, as a key part of the ceramic membrane [8], and its properties (e.g., permeability, surface) greatly depend on the coating process, which mainly affect the pore-size, porosity, and pore-size distribution of the ceramic membrane [9–12].

The rapid development of petrochemical, biological, pharmaceutical, and other high value-added industries also requires high-performance ceramic membranes [13]. Traditionally, ceramic membranes are formed by dip-coating on the surface of the ceramic support. The slurry of ceramic membranes plays an important role in the dip-coating process, which mainly consists of ceramic powders, binders, plasticizers, and other additives [14,15]. At present, in order to prepare high-performance ceramic membranes, some researchers often control the slurry performance [16] (e.g., viscosity and solid content) or the coating time. However, an uneven porosity and roughness of the support makes different parts of the same membrane tube perform differently, and there are also certain defects, especially in long multichannel tubular ceramic membranes. For this reason, some researchers have studied the coating process of long multichannel tubular ceramic membranes in detail. These researchers' studies are as follows:

Table 1 shows the preparation process for ceramic membranes. It can be seen that most ceramic membranes are prepared by the dip-coating method, two-step coating, and sintering methods. However, the preparation process is complex, and it also produces defects, although this involves one-step sintering. Meanwhile, it also leads to an uneven surface, a high cost, and a ceramic membrane with low performance and efficiency. Thus, it limits the industrial application of ceramic membranes.

Table 1. Preparation process of ceramic membranes.

Coating Process	Advantages and Disadvantages	Authors and Literature
Dip-coating process. The support is placed vertically, and the suspension is driven by a pump to maintain the flow inside the support's inner cavity at a certain flow velocity, One-step coating and sintering is used.	It is easy to operate with high efficiency, but the performance of the ceramic membranes depends on the pump power and the support properties. However, this leads to different parts having uneven membrane thicknesses.	Zhu, J. [17]; Fan, Y.; Xu, N. "Modified dip-coating method for preparation of pinhole-free ceramic membranes"
Dip-coating process, two-step coating and one-step sintering. A layer of organic material is coated, and then the separate layer of slurry is coated.	Low cost and high efficiency are the advantages of the process, but the viscosity of the organics and the sintering system have a great influence on the bonding properties of the ceramic membranes. It is much harder to industrialize.	Chen, X. [18]; Lin, Y.; Lu, Y. "A facile nanoparticle doping sol–gel method for the fabrication of defect-free nanoporous ceramic membranes"
Dip-coating process, boehmite sol mixed with alumina particles as the membrane slurry, two-step coating and one-step sintering.	The process is highly efficient and has a low cost. However, the stability of the slurry is difficult to control, and the process is complex. It is easy to identify membrane defects, but hard to industrialize.	Zou, D. [19]; Qiu, M.; Chen, X.; Fan, Y. "One-step preparation of high-performance bi-layer α-alumina ultrafiltration membranes via co-sintering process"
Dip-coating process, sol-gel method, two-step coating, and two-step sintering.	The performance of the membrane is high, and the preparation has a high cost. It has low efficiency, and the process is complex.	Bayat, A. [20]; Mahdavi, H.; Kazemimoghaddam, M. "Preparation and characterization of γ-alumina ceramic ultrafiltration membranes for pretreatment of oily wastewater"

This paper aims to provide a convenient and efficient coating process to prepare ceramic membranes by the two-step coating method, with a high viscosity flush after a low viscosity coating, using one-step sintering. The effects of the solid content and coating time on the properties of the ceramic membrane were investigated in detail. Compared with the one-step coating process, this method had considerable advantages in eliminating cracking and uneven surfaces on the ceramic membranes. Furthermore, this method can enhance the permeability of defect-free ceramic membranes.

2. Materials and Methods

2.1. Preparation of Membranes

Porous alumina tubular supports (19-channel; outer diameter of 30 mm and the length of 1200 mm) was chosen for the foundation. The average pore size was about 4 μm, and its porosity was 40%.

The stable coating slurry was prepared as follows: the alumina powders (Luoyang, He'nan, China, Purity ≧ 99%) were used without further treatment; the particles size distribution of alumina powders is shown in Figure 1. The alumina was dispersed in pure water, Dolapix CE-64 as a dispersant was added, and the addition amount was 0.05 wt % of the powder mass. The suspension was mixed with a ball mill at 150 rpm for 3 hr with different solid contents of 5 wt %, 6 wt %, 7 wt %, and 14 wt %. Then, an aqueous solution of 30 wt % or 38 wt % Polyvinyl Alcohol (12% concentration, PVA-1799) was added as a binder. This suspension was ball milled for 2 hr to prepare the stable ceramic membrane slurry. In ball milling, the mass ratio of powder/alumina ball/alcohol was 1:1:1.8. The process is shown in Figure 2.

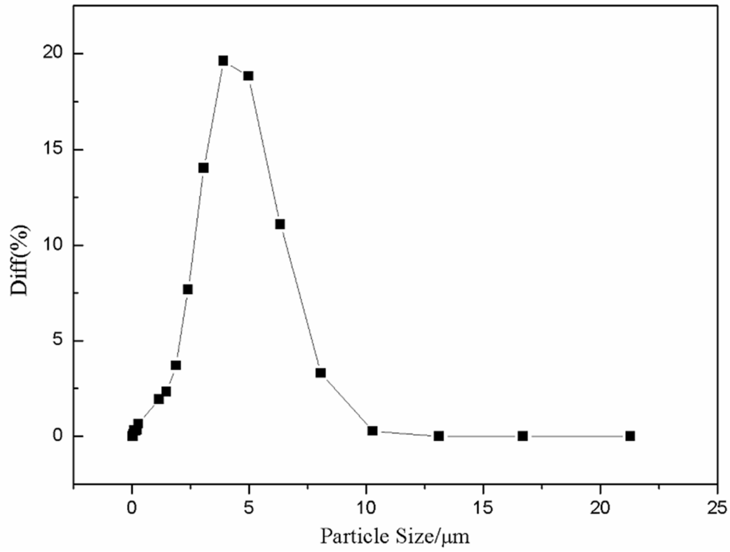

Figure 1. Particle size distribution of alumina powders.

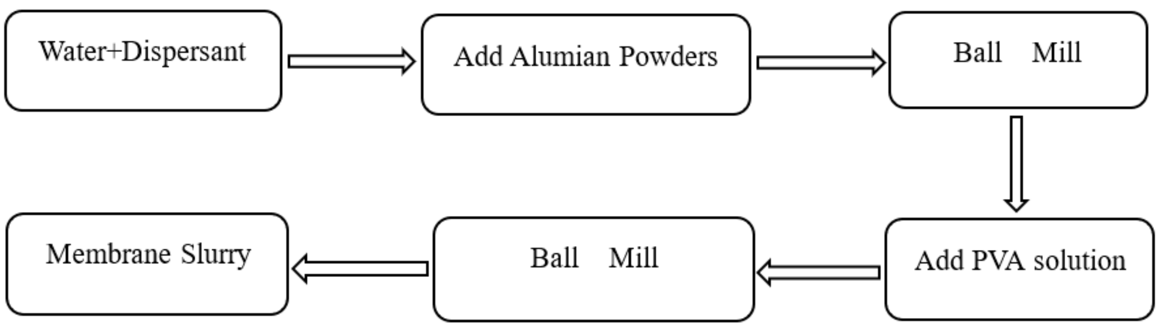

Figure 2. Preparation process of the ceramic membrane slurry.

(1) One-step coating process:

The support was placed vertically and filled with suspension with 14 wt % solid content, 30 wt % PVA solution with a viscosity of 40 Pa.s. The coating time was 20 s, and the superfluous suspension was discharged from the bottom using the effect of gravity.

(2) Two-step coating process:

The preparation process was similar to that in the traditional coating process. The difference was that the coated membrane needed to be flushed again after the one-step coating process. The solid content was 5~7 wt %, the content of the PVA solution was 38 wt %, and the viscosity was 55 Pa.s. Then, the support was placed horizontally, and the suspension was placed in a 2 m high storage tank. The flow rate of the slurry was 0.8 m/s.

Finally, the samples were dried at room temperature for 48 hr, and then sintered at 1450 °C for 2 hr under normal temperature and pressure, and the ceramic membrane was formed.

2.2. Characterization of the Membranes

The surface and cross-sectional morphologies of the membranes were analyzed by using fleid emitting scanning electron microscopy (FE-SEM, JSM-6700F, JEOL, Tokyo, Japan).

Pore size distribution (PSD) of the membranes were obtained by a pore size distribution analyzer (PSDA-20, GaoQ Functional Materials Co., Ltd. Nanjing, China).

The water flux of the membrane was tested in a cross-flow filtration apparatus. The apparatus was capable of operating at a variety of temperatures and pressures. During the test, the volume of the water permeating the membrane and the collection time were recorded.

The viscosity was tested by a rotor viscometer (BLF2-DV-II-ZZ).

The particle size distribution of the alumina powders was measured by a laser particle size analyzer (Bettersize2000, Dandong, China).

3. Results and Discussion

3.1. Effect of the Preparation Process on the Properties of the Ceramic Membrane

As a porous ceramic membrane, the separation layer was prepared by alumina powder accumulation. The pore size or its distribution depended on the state of alumina powder accumulation. The pore size was greater when the state of the alumina powder accumulation was loose. On the contrary, the pore size was smaller. Figure 3 shows the pore-size distribution of a ceramic membrane with 5 wt % solid content. As can be seen, the one-step coating method displayed a double-peak in the pore-size distribution, and the two-step coating method showed a single peak. This implied that the surface of the ceramic membrane prepared by the two-step coating method was smooth, but defects on the membrane surface were caused by the one-step coating method. The reason for this result was that when the slurry was coated, the solid powder was deposited onto the surface of the support, due to the actions of capillary force and viscosity [21]. However, because of the inhomogeneity of the pore-size of the support and the effect of the bubbles in the slurry, the membrane layer produced a large hole-defect. However, based on the one-step coating method, it was flushed by a second coating, due to the higher viscosity and the action of the osmotic pull force [22]. The membrane layer was smooth and without defects.

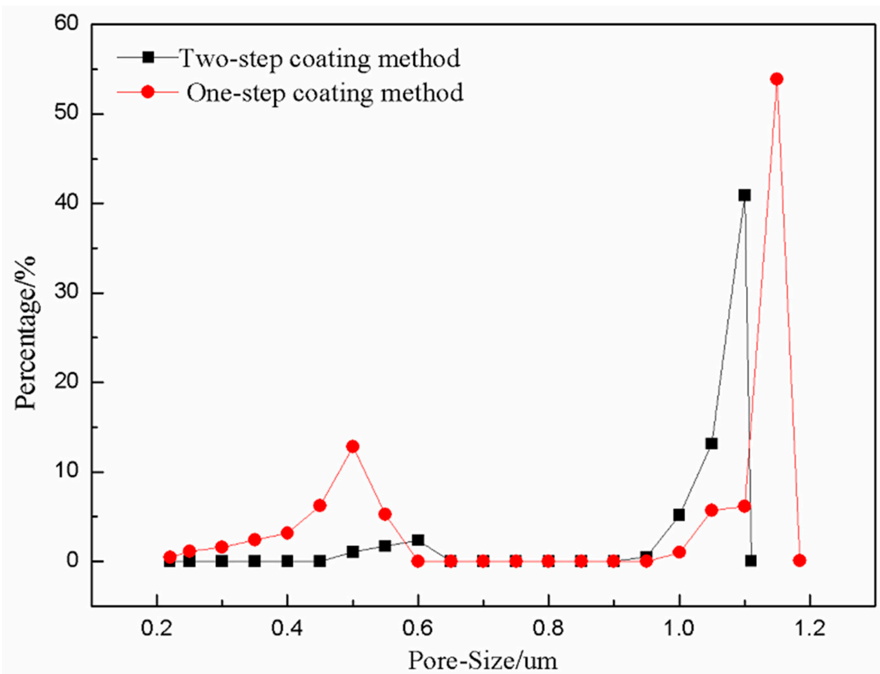

Figure 3. Pore-size distribution of ceramic membrane with 5 wt % solid content.

Figure 4 shows a schematic diagram of the coating. Defects of the membrane were produced by the first coating, and repaired during the second coating. Figure 5 shows the SEM images of the samples prepared by different coating methods. Obviously, the surface of the ceramic membrane had an amount of hole-defects produced by the one-step coating method, and the two-step coating method produced a smooth surface. This further verified the above explanation and the appearance of the coating. Consequently, the effect of the solid content and coating time on the properties of the ceramic membrane prepared by the two-step coating method was studied in detail.

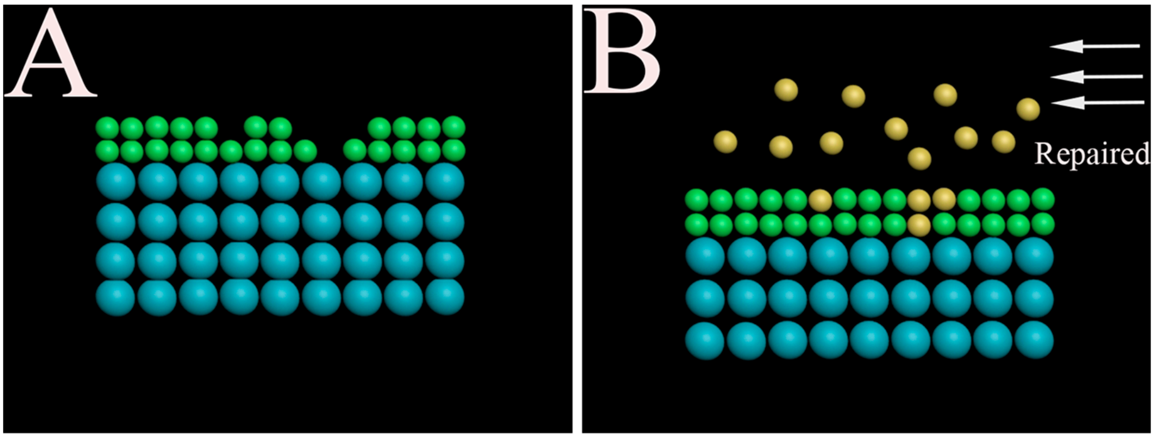

Figure 4. Schematic diagram of coating with different coating methods (**A**: one-step coating; **B**: two-step coating).

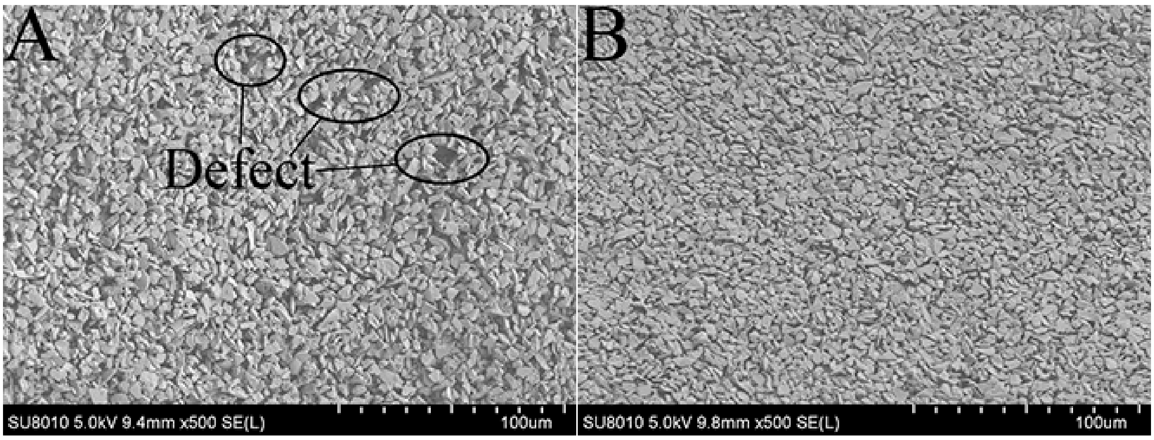

Figure 5. SEM images of the samples prepared by different coating methods. **A**—One-step coating method; **B**—Two-step coating method.

3.2. Effect of the Solid Content on the Properties of the Ceramic Membrane

Figure 6 shows the pore-size distribution of the ceramic membrane with different solid contents, prepared by the two-step coating method, with a coating time of 11 s. As can be seen from the Figure 6, within a certain time range, as the solid content increased, the maximum pore size of the ceramic membrane decreased, and the average of the pore size gradually decreased. This indicated that the two-step coating method can improve the performance of the ceramic membrane for a certain period of time.

As discussed above, the membrane layer was prepared for the alumina powder accumulation. When the supports were dip-coated, due to the action of the capillary, a wet membrane layer of a certain thickness formed. As the solid content increased, the alumina powder increased to the same volume as that of the slurry. Furthermore, the thicknesses of the alumina deposited onto the surface of the support increased, due to the force of the capillary. There were two main reasons for the decrease of the average pore size and the maximum pore size. On the one hand, as the solid content increased, Al_2O_3 particles repaired the defects of the ceramic membrane over a certain time. Thus, the surface of the ceramic membrane was even, which reduced the defects of the membrane, and made the average pore size smaller. On the other hand, according to the dynamic flow, which analyzed the coating fluid during the membrane coating process, the function f (h) expresses the membrane thickness given by Landau and Levich [23]:

$$h = 0.944\left(\frac{\eta\nu_\omega}{\gamma}\right)^{\frac{1}{6}}\left(\frac{\eta\nu_\omega}{\rho g}\right)^{\frac{1}{2}}$$

where ν_w is the relative speed of the slurry movement, η is the suspension viscosity; ρg is the gravity; γ is the surface tension. It can be seen that the thickness of the ceramic membrane is proportional to the viscosity of the suspension, and the higher the solid content, the greater the relative viscosity of the slurry. Therefore, the thickness of the ceramic membrane increased, and the average pore size of the ceramic membrane decreased.

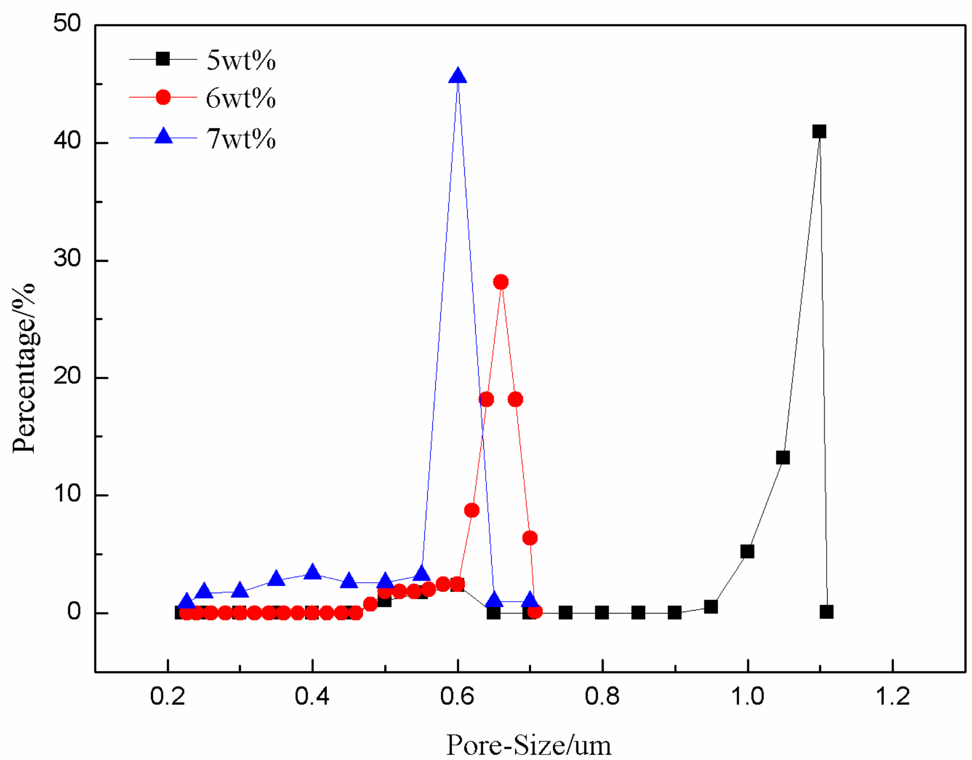

Figure 6. Pore-size distribution of the ceramic membrane with different solid contents.

3.3. Effect of Coating Time on the Properties of the Ceramic Membrane

Figure 7 shows the pore-size distribution of the ceramic membrane with different coating times, prepared by the two-step coating method, and the solid content is 7 wt %. As can be seen, with a coating time of between 5 s and 11 s, the average pore-size of the ceramic membrane decreased. However, when the coating time exceeded 11 s, with a maximum of 17 s, the pore size of the ceramic membrane increased.

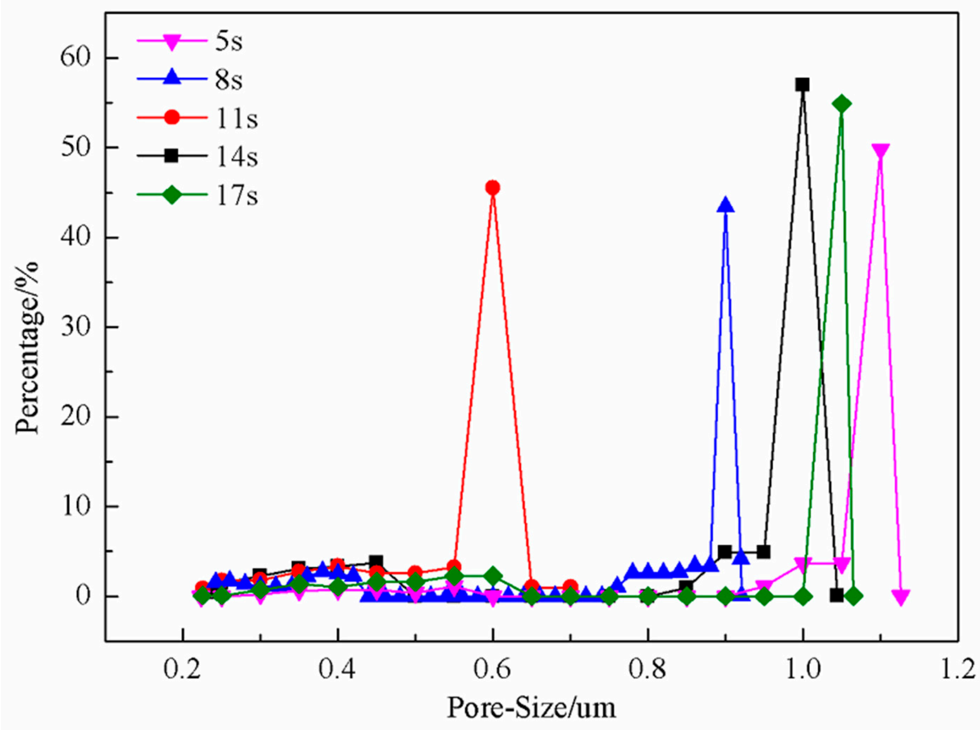

Figure 7. Pore-size distribution of the ceramic membrane with different coating times.

The main reason for this phenomenon was that Al_2O_3 particles repaired the big hole during two-step coating. Thus, the largest hole was reduced, the thickness of the ceramic membrane increased, and the pore-size decreased evenly. However, by extending the coating time, the Al_2O_3 particles moved far away from the support body, and the wet membrane layer became loose. Meanwhile, it was easy to separate it from the wet membrane layer, using the flowing slurry, for a short period of time. In addition, the Al_2O_3 deposition on the surface of the wet membrane was lower, and the big hole repair was incomplete. As the coating time increased, the wet membrane far away from the support could be diffused back into the slurry, causing damage to the membrane structure. The thickness of the ceramic membrane decreased, or the surface of the ceramic membrane was uneven. Furthermore, the pore size of the ceramic membrane increased.

Figure 8 shows SEM images of the ceramic membrane with different coating times. It can be seen from Figure 8 that, with a coating time ranging from 5 s to 11 s, the thickness of the ceramic membrane increased, the surface of the ceramic membrane was smooth, or the distance of the alumina particles decreased. So, the pore size of the ceramic membrane decreased. On the contrary, as the coating time extended from 11 s to 17 s, the thickness of the ceramic membrane decreased, the surface of the membrane was uneven, or the distance of the alumina particle increased. This made the pore size of the ceramic membrane gradually increase.

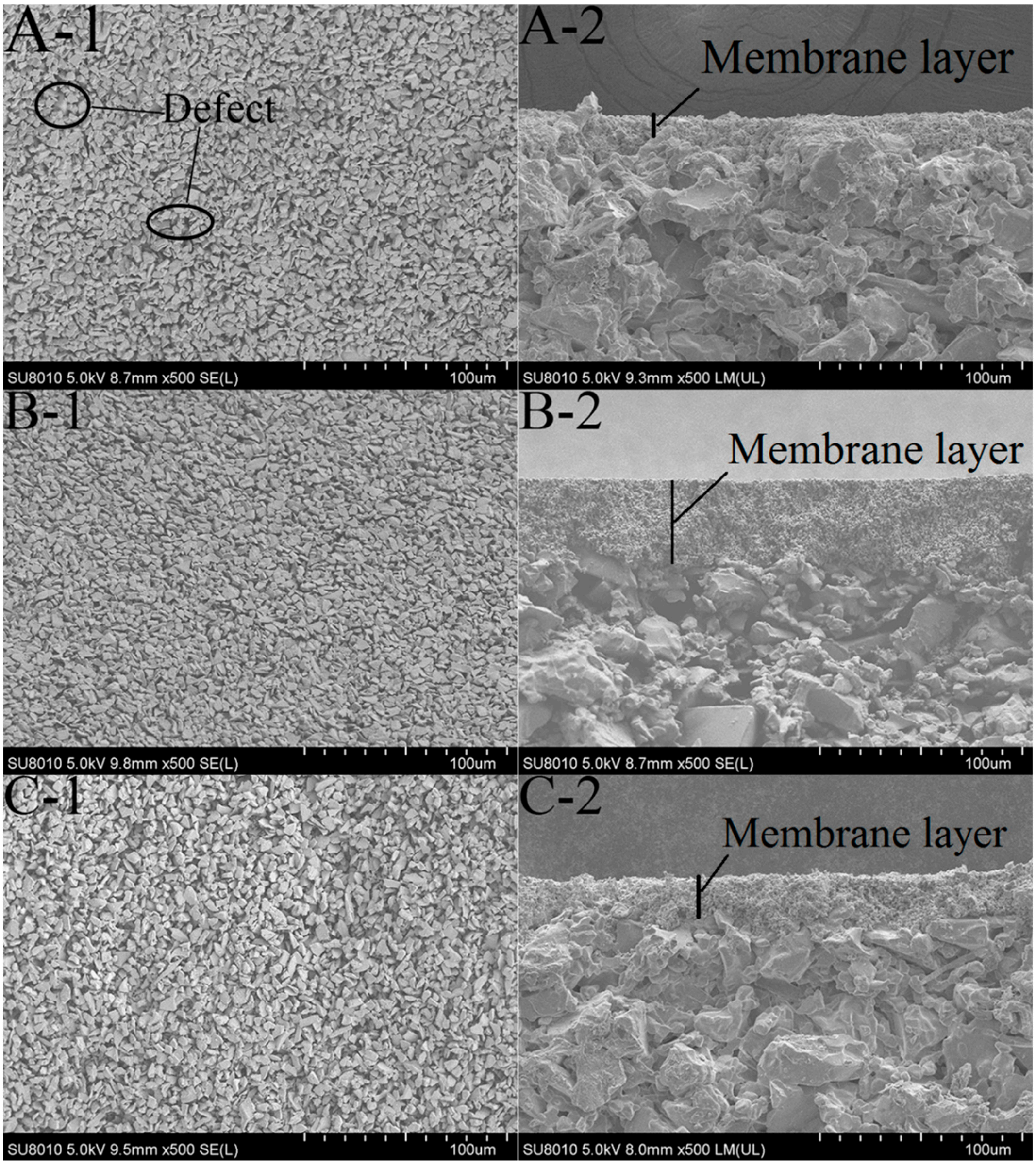

Figure 8. SEM images of the samples with different coating times (**A**—5 s, **B**—11 s, **C**—17 s; **A-1**, **B-2**, **C-1** are surface images, and **A-2**, **B-2**, **C-2** are cross-sectional images).

3.4. Permeating Flux of the Ceramic Membrane

Figure 9 shows the permeating flux of the ceramic membranes produced by one-step sintering at 1450 °C for 2 hr with 5 wt % solid content and a coating time of 11 s by the two-step coating method. It can be seen from Figure 9 that the water flux of the ceramic membrane prepared by the two-step coating method had a linear relationship with the pressure. The water permeating flux had a constant range of 0.1–0.5 Mpa. It reflected that the ceramic membrane had an even membrane surface, and a high permeability, due to the low tortuosity [24]. What is more, the Hagen Poiseuille equation [25] also explains the permeability of the porous structures:

$$J = \frac{\varepsilon}{\tau}\frac{r^2}{8\eta}\frac{\Delta P}{\Delta x}$$

where ε is the porosity, τ is the tortuous degree, r is the aperture of the membrane, η is the permeable medium viscosity, ΔP is the trans-membrane pressure difference, and Δx is the thickness of the membrane layer. It further proved that the pore tortuosity, surface uniformity, porosity, and permeability of the ceramic membrane prepared by the two-step coating method was better. The reason was that the thickness of the ceramic membrane prepared by the two-step method was even, which led to consistency between the pore size and the pore curvature. Under a certain pressure, the permeabilities of various parts of the ceramic membrane were consistent.

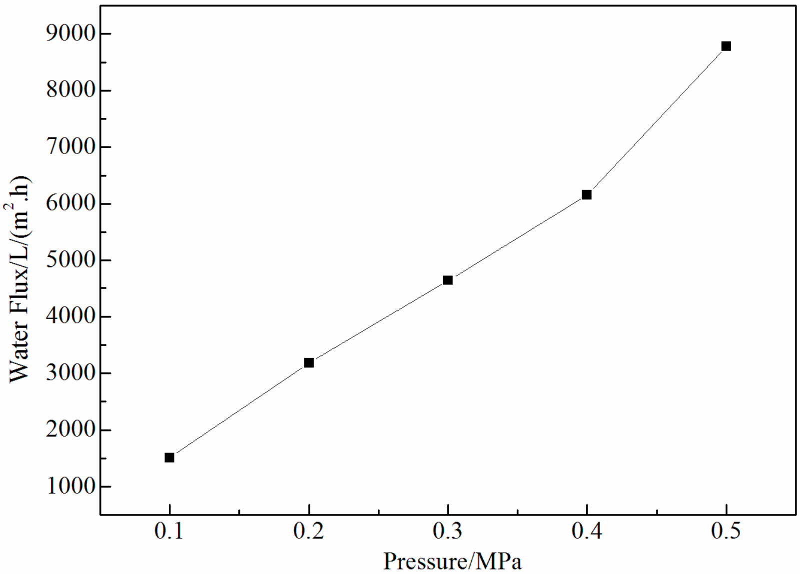

Figure 9. Water-permeating flux of the ceramic membrane.

4. Conclusions

The effects of the two-coating process by the one-step coating method and the two-step method on the properties of the porous ceramic membrane are comparatively investigated. The process of coating has an important effect on the property of the porous alumina membranes. The pore-size distribution of the ceramic membrane prepared by the two-step coating method is more even than that prepared by the one-step coating method, due to the action of the osmotic pull force with the alumina particles. What is more, the properties of the membrane surface are better than those of the membrane prepared by the one-step coating method. As the solid content increases, the pore-size decreases; as the coating time increases, the pore-size first decreases and then increases gradually during coating by the two-step coating method. The high-performance ceramic membrane was been obtained by one-step sintering at 1450 °C for 2 hr, with 7 wt % solid content, and prepared by the two-step coating method, with a coating time of 11 s. As a result, the thickness of the membrane is 30 μm, the average of pore size is 0.6 μm, and the water flux is 1513 L/(m^2·h·bar). It may be a better method to prepare the ceramic membrane by the one-step sintering and the two-step coating method, with a high viscosity flush after low-viscosity coating.

Author Contributions: Z.H. designed the experiments, performed the experiments, and wrote the paper. Y.Y. analyzed the data and wrote the paper. F.L. and Q.C. performed part of the experiments. Y.W. and J.R. modified the paper for grammar.

Funding: This research was funded by National Natural Science Foundation of China (No. 21761015, 51662020 and 51772136), Jiangxi Provincial Department of Science and Technology (No. 20165BCB19014), Education Department of Jiangxi Province (GJJ170808 and GJJ170778) and Jingdezhen City Bureau of Science and Technology (No. 20161GYZD011-017).

Acknowledgments: The authors gratefully acknowledge the discussion of Jian-er Zhou.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Sarkar, S.; Bandyopadhyay, S.; Larbot, A.; Cerneaux, S. New clay–alumina porous capillary supports for filtration application. *J. Membr. Sci.* **2018**, *392*, 130–136. [CrossRef]
2. Shkrabina, R.A.; Boneckamp, B.; Pex, P.; Veringa, H.; Ismagilov, Z. Porous structure of alumina ceramic support for gas separation membranes, II. Study of porous structure of ceramic composition. *React. Kinet. Catal. Lett.* **1995**, *54*, 193–201. [CrossRef]
3. Dong, Y.; Chen, S.; Zhang, X.; Yang, J.; Liu, X.; Meng, G. Fabrication and characterization of low cost tubular mineral-based ceramic membranes for micro-filtration from natural zeolite. *J. Membr. Sci.* **2006**, *281*, 592–599. [CrossRef]
4. Bao, Q.; Dong, W.; Zhou, J.; Wang, Y.; Liu, Y. Effects of pore former on properties of alumina porous ceramic for application in micro-filtration membrane supports. *Key Eng. Mater.* **2015**, *655*, 97–102. [CrossRef]
5. Wang, F.; Ye, J.; He, G.; Liu, G.; Xie, Z.; Li, J. Preparation and characterization of porous $MgAl_2O_4$ spinel ceramic supports from bauxite and magnesite. *Ceram. Int.* **2015**, *41*, 7374–7380. [CrossRef]
6. Hubadillah, S.; Othman, M.; Matsuura, T. Fabrications and applications of low cost ceramic membrane from kaolin: A comprehensive review. *Ceram. Int.* **2018**, *44*, 4538–4560. [CrossRef]
7. Yin, X.; Guan, K.; Gao, P. A preparation method for the highly permeable ceramic microfiltration membrane—Precursor film firing method. *RSC Adv.* **2018**, *8*, 2906–2914. [CrossRef]
8. Guo, H.; Li, W.; Ye, F. Low-cost porous mullite ceramic membrane supports fabricated from kyanite by casting and reaction sintering. *Ceram. Int.* **2016**, *42*, 4819–4826. [CrossRef]
9. Bruggen, B.; Vandecasteele, C.; Gestel, T. A review of pressure-driven membrane processes in wastewater treatment and drinking water production. *Environ. Prog. Sustain.* **2010**, *22*, 46–56. [CrossRef]
10. Yanagishita, H.; Kitamoto, D.; Haraya, K. Separation performance of polyimide composite membrane prepared by dip coating process. *J. Membr. Sci.* **2001**, *188*, 165–172. [CrossRef]
11. Ding, X.; Fan, Y.; Xu, N. Modeling and control of ceramic membrane thickness during dip-coating process. *J. Chem. Ind. Eng.* **2006**, *57*, 1003–1008. (In Chinese) [CrossRef]
12. Yan, H.; Lu, X.; Wu, C. Fabrication of a super-hydrophobic polyvinylidene fluoride hollow fiber membrane using a particle coating process. *J. Membr. Sci.* **2017**, *533*, 130–140. [CrossRef]
13. Chang, Q.; Yang, Y.; Zhang, X.; Wang, Y.; Zhou, J.; Wang, X.; Cerneaux, S.; Zhu, L.; Dong, Y. Effect of particle size distribution of raw powders on pore size distribution and bending strength of Al_2O_3, microfiltration membrane supports. *J. Eur. Ceram. Soc.* **2014**, *34*, 3819–3825. [CrossRef]
14. Liu, Y.; Zhu, W.; Guan, K. Preparation of high permeable alumina ceramic membrane with good separation performance via UV curing technique. *RSC Adv.* **2018**, *8*, 13567–13577. [CrossRef]
15. Sun, C.; Zhang, J.; Jiang, W. Study on preparation of ultrafine separation membrane on porous alumina supporters. *Inorg. Chem. Ind.* **2010**, *42*, 17–20. (In Chinese) [CrossRef]
16. Samei, M.; Mohammadi, T.; Asadi, A. Tubular composite PVA ceramic supported membrane for bio-ethanol production. *Chem. Eng. Res. Des.* **2013**, *91*, 2703–2712. [CrossRef]
17. Zhu, J.; Fan, Y.; Xu, N. Modified dip-coating method for preparation of pinhole-free ceramic membranes. *J. Membr. Sci.* **2011**, *367*, 14–20. [CrossRef]
18. Chen, X.; Lin, Y.; Lu, Y. A facile nanoparticle doping sol–gel method for the fabrication of defect-free nanoporous ceramic membranes. *Colloid Interface Sci. Commun.* **2015**, *5*, 12–15. [CrossRef]
19. Zou, D.; Qiu, M.; Chen, X.; Fan, Y. One-step preparation of high-performance bi-layer α-alumina ultrafiltration membranes via co-sintering process. *J. Membr. Sci.* **2017**, *524*, 141–150. [CrossRef]
20. Bayat, A.; Mahdavi, H.; Kazemimoghaddam, M. Preparation and characterization of γ-alumina ceramic ultrafiltration membranes for pretreatment of oily wastewater. *Desalin. Water Treat.* **2016**, *57*, 1–11. [CrossRef]
21. Islam, M.; Stoicheva, R. An investigation on the capillary viscosities of some hydrophilic fluids permeating through a poly(vinyl chloride) membrane. *J. Membr. Sci.* **1994**, *92*, 209–215. [CrossRef]
22. Choudhury, P.; Ranawat, M.; Chauhan, C. Asymmetric membrane capsule for osmotic delivery of flurbiprofen. *Acta Pharm.* **2007**, *57*, 343–350. [CrossRef] [PubMed]

23. Levich, V. Physicochemical Hydrodynamics. *Phys. Today* **1963**, *16*, 75. [CrossRef]
24. Yang, Y.; Chang, Q.; Hu, Z.; Zhang, X. A Comparative Study on the Addition Methods of TiO_2 Sintering Aid to the Properties of Porous Alumina Membrane Support. *Membranes* **2018**, *8*, 49. [CrossRef] [PubMed]
25. Bissett, H.; Zah, J.; Krieg, H. Manufacture and optimization of tubular ceramic membrane supports. *Powder Technol.* **2008**, *181*, 57–66. [CrossRef]