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A review of preparation techniques of porous ceramic membranes

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Porous ceramic membranes with their various advantages, such as better thermal, chemical and mechanical resistance, controllable micro-structure and little pollution to our environment, have been attracting much attention in the scientific community recently. With the development of technology, lowering the cost of ceramic membranes and prepare membranes with high permeability, high selectivity is becoming more important. The advances in the past ten years in techniques are reviewed. Finally, prospect of ceramic membranes was predicted.

Key words: Ceramic membranes, Preparation methods, High selectivity, Prospect.

Introduction

Nowadays, with strong environmental demands, porous ceramic membranes should be leading candidates for applications such as massive liquid waste pre-treatment, strong acidic or alkaline media separation and thermal shock separation applications, but they cannot be used on a large scale in industry due to their several drawbacks such as high cost, rare membrane materials and narrow application range. In recent years, porous ceramic membranes have attracted much attention in the scientific community for their outstanding merits such as species diversity and novel additional properties [1-3].

Porous ceramic membrane separation performance and materials and distribution of pore size, porosity, pore morphology microstructure has a close relationship. Pore size of the porous ceramic membrane can be several nanometers to several tens of microns range modulation. Compared with a porous ceramic, porous asymmetric ceramic membrane structures own higher separation performance [4]. Film thickness is generally between several tens of nanometers to hundreds of microns, can be from nanoscale screening (eg nanofiltration membrane multivalent ions high retention rate) to a visible separation of large particles (such as high temperature gas dust removal), with a wide range of applications [5]. porous ceramic membrane separation layer hole in any stacked structure formed particles, the porosity is usually from 30% ~ 35% [6], and the winding factor regulation is more difficult, which makes a substantial increase in the ceramic membrane performance was limited. Preparation of ceramic membrane technology to improve its permeability and ceramic membrane permeation selectivity is one of the key areas of research. How to further reduce the cost of preparing ceramic membrane ceramic membrane preparation is also one of the key research areas.

In this paper, the field of ceramic membrane over the past decade numerous research focus, a broad overview of domestic and foreign researchers in the preparation of a high permeability, high selectivity and low cost ceramic membrane permeability preparation technology and other aspects of research.

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Research on Preparation Techniques of Highly Permeable Ceramic Membrane

Ceramic membrane permeability depends primarily on its porosity, pore tortuosity and pore morphology. Pore and fiber build method is a method for preparing high permeable ceramic membrane current mainstream technology. Pore method by adding the number of holes to allow the expansion, thereby enhancing the porosity of the ceramic membrane [7]. Template method is a special kind of pore forming agent method, the pore-forming agent having a specific pore size and shape so ordered, also increase its porosity. Ceramic fiber structures rule film fiber as raw material, through the layers of the fiber structures to make holes Diversification of channels, in order to achieve increased porosity.

Pore method

Pore method is to improve the porosity of the porous ceramic a simple and economical method of pore-forming agent can be divided into inorganic and organic types. Inorganic pore-forming agent are ammonium carbonate, ammonium bicarbonate and

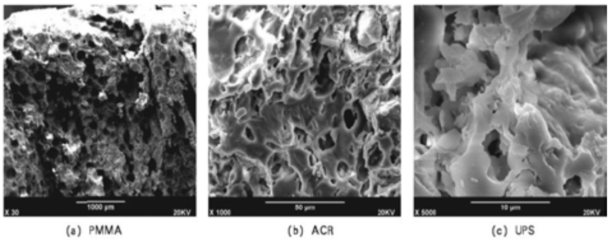


Fig. 1. The morphology of porous ceramics obtained via different pore-forming agent (a pore-forming agent in an amount of 10 wt%) [7].

ammonium chloride salts or other high temperature decomposable inorganic carbon such as graphite, coal ash, etc.; organic pore-forming agent include natural fibers, polymers, such as sawdust, shell flour, starch, polystyrene (PS), polymethyl methacrylate [8-11]. Figure 1 showed the morphology of porous ceramics obtained via different pore-forming agent.

Shao *et al*. [12] prepared porous 20 vol. % BN/Si_3N_4 composite ceramics with different volume fractions of 32.5%to 45.8% in porosity by adding different amounts of PMMA spheres as the pore-forming agent. Cruz et al. [13] fabricated macroporous nanocrystalline 4 mol% yttria-stabilised zirconia ceramics by a novel colloidal processing technique, using a commercially available nano-powder with modified surface and polymethylmethacrylate (PMMA) sacrificial templates as starting materials. Liu and Wang [14] successfully fabricated porous yttria-stabilized zirconia (YSZ) ceramics by the dry pressing method with different size (1.8-20 μm) and amount (2-60 vol. %) of mono-dispersed poly methyl methacrylate (PMMA) micro-balls. Xia *et al*. [15] prepared porous Si_3N_4 ceramics using PMMA as pore former, and the mechanical and dielectric properties were investigated, as a function of porosity.

Wang *et al*. [16] took SiC particles whose mean grain size is 2.4μm as the main raw materials, activated carbon and graphite as pore former, and adds ceramic binder and Sodium carboxymethyl cellulose (CMC) solution, mixed to shape with the coated process step by step. Sarikaya and Dogan [17] addressed a detailed and systematic comparison of different pore formers (e.g. graphite, polymethyl methacrylate, sucrose and polystyrene) with distinct features such as size, distribution and morphology of particles and decomposition/oxidation behavior.

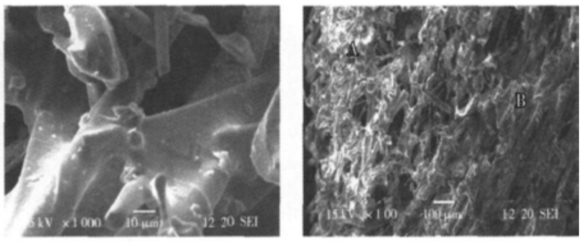
Yang and Tsai [18] first used the Atterberg limits tests for understanding the effects of starch addition to the plasticity of paste. Topateş *et al*. [19] studied the possibility of enhancing permeability of porous Si_3N_4 ceramics by using pore former additive (potato starch; 0-30 vol.%). The open porosity of samples changed between 52 and 66% as the mean pore channel size values ranged from 0.9 to 4 μm. Increasing starch addition provides bimodal distribution of pore size channels by accompanying abrupt increment in non-Darcian permeability. k_2 value rised from 8.7×10^{-10} m to 30.1×10^{-10} m. Živcová *et al*. [20] studied the elastic properties, in particular the tensile modulus (Young's modulus) and Poisson ratio, of porous alumina, zirconia, and alumina-zirconia composite ceramics using the resonance frequency method and the results compared with theoretical predictions. Starch is used as a pore-forming agent, so that the resulting microstructure is essentially of the matrix-inclusion type (with large bulk pores, connected by small throats when a percolation threshold is exceeded). Guo *et al*. [21] prepared porous SiC ceramics by pressureless sintering, using silicon carbide micron powder as raw material, alumina and yttria as fluxes and starch as pore-forming agent. Results show: with the increase of the content of pore-forming agent, the density and strength of the SiC ceramics decrease but the porosity increases; the content of poreforming agent makes no difference to phase composition of SiC ceramics.

Fiber structures technology

The fibers in the forming process on the surface of the support can quickly bypass due to its slim configuration, significantly reducing the infiltration within the membrane [22], and is easy to obtain a high porosity and specific surface area; the permeability of the membrane material has a significant role to improve [23].

Liang and Weng [24] investigated porous hydroxyapatite (HA) ceramic fabricated by 3D fiber network. The results showed that the pore characteristics and the inner structure of the sample made from this technique have settled for essential requests of porous bioceramic. The channels in sintered scaffold shown in SEM (scanning electron microscopy) micrographs have directional connection, equal distribution, intact configuration and existence of thin stripes on inner walls. All of these characteristics have met requests for tissue cell developing, transplanting and attaching. Ma *et al*. [25] studied fiber reinforced ceramic composite (mullite fiber/ α-Al2O3 powder) produced by the organic flocculating method. Air-quenching was employed to determine the drop in bending strength of the composite after thermal shock, and the critical temperature of the composites with different fiber contents. The thermal shock behavior was found to improve significantly by the addition of 3% hexagonal boron nitride (H-BN). The critical temperature reached up to 1000 °C, compared to 500 °C without presence of BN.

Zhou *et al*. [26] prepared alumina fiber reinforced porous ceramics by adding plasticizers and pore-forming agents by the way of extrusion forming. The results show that the contractibility of the material decreases and the porosity and the flexural strength of the material first increase and then decrease with the increasing of the sintering temperature and the alumina fiber content. Isobe *et al*. [27] prepared porous alumina



(a) Ceramic fibers bonded to each other **(b) Section of the samples**

Fig. 2. SEM photos of fibrous porous ceramic [29].

ceramics with unidirectionally oriented pores using an extrusion method. The paste for extrusion was prepared by mixing alumina and nylon 66 fibers with binder and dispersant. The degree of orientation of the cylindrical pores was evaluated from SEM micrographs to be highly aligned to the extrusion direction. The orientation of the pores decreased with increasing fiber loading because of strong interaction between the fibers. The pore size distribution of the extruded samples showed a peak at 16 μm corresponding to the cylindrical pore diameter and also at 4 and 6 μm corresponding to the pores formed by connection of the fibers. Ke *et al*. [28] overcome the structural deficiencies by constructing hierarchically structured separation layer on a porous substrate using larger titanate nanofibres and smaller boehmite nanofibres. These membranes are able to effectively filter out species larger than 60 nm at flow rates orders of magnitude greater than conventional membranes. The retention can attain more than 95%, while maintaining a high flux rate about 900 L m^{-2} h. The calcination after spin-coating creates solid linkages between the fibres and between fibres and substrate, in addition to convert boehmite into λ-alumina nanofibres. Liu *et al*. [29] fabricated the fibrous porous ceramic fiber with different diameters for purifying high temperature dust gas by one step with pore-gradient structure. Results showed that the suitable preparing conditions were as follows: the temperature of 800°C, the rupture strength of 6.7 MPa, and the porosity of 76%. The permeation resistance of the sample was 96 Pa (at the room temperature) on the air rate of 1 m/min, and the sample resistance decreased with the rising of firing temperature. Fig. 2 is the SEM photos of fibrous porous ceramic.

Fiber layer structures with high porosity increased through the permeate flux, but reduces the strength of the film. Thus, strengthen the neck connecting the fibers to improve the strength of the fiber membrane is needed.

Fernando and Chung [30] prepared alumina fiber based filter membranes using acid phosphate (phosphoric acid plus aluminum hydroxide), colloidal alumina, monoaluminum phosphate and three types of colloidal silica binders at various binders contents. The filter membranes containing between 5% and 10% by weight of acid phosphate binder exhibited the highest flexural strength, compressive strength, work of fracture and elastic modulus in comparison to those containing the other binders at equivalent binder contents, and exhibited the lowest pressure drop in comparison to membranes with other binders and having equivalent flexural and compressive strengths. Qiu *et al*. [31] briefly described the preparation of titania ultrafiltration membranes with intermediate layer of sol-coated nanofibers. In this process, titiania nanofibers cover on the porous substrate to produce uniform layer with high porosity and flux. The use of titania nanoparticles from sol has been found to bring an improvement on the mechanical strength of the titania nanofiber membrane due to the formation of sintering neck between nanofibers with colloidal particles (sol) at lower sintering temperature. In order to reduce the pore size and achieve high separation efficiency, titania colloidal particulate sol is used to coat on the top of the titania nanofiber layer and then co-sintered at the suitable sintering temperature of the titania gel (480 ºC) to prepare ultrafiltration membranes. Fig. 3 showed the morphology of titania nanofibers sintered at different temperature.

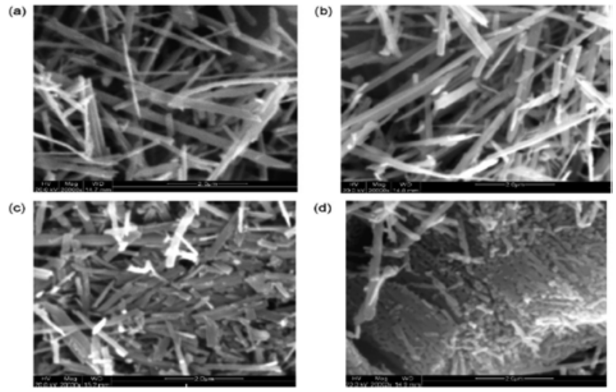


Fig. 3. The morphology of titania nanofibers sintered at different temperature: (a) raw material, (b) 400 ºC, (c) 600 ºC, (d) 800 ºC.

Template method

Template method is a method can be precisely controlled pore structure, pore size and distribution technology. At present, there are several ways:

(1) Porous media- situ reactive method:

Aoki and Mcenaney [32] directly prepared porous SiC by the silicon gas and porous carbon, and shape of porous SiC is kept as porous carbon. Zhang *et al*. [33] fabricated porous alumina ceramics with unidirectionally aligned continuous pores via the slurry coating of fugitive fiber. Cotton thread was coated with ceramic slurry by pulling it through the slurry, and specimens were produced by spooling the coated thread. The obtained porous alumina ceramics had an average pore diameter of 165 μm, 35% open porosity, and a bending strength of 160 MPa. Fig. 4. is the flow diagram of the

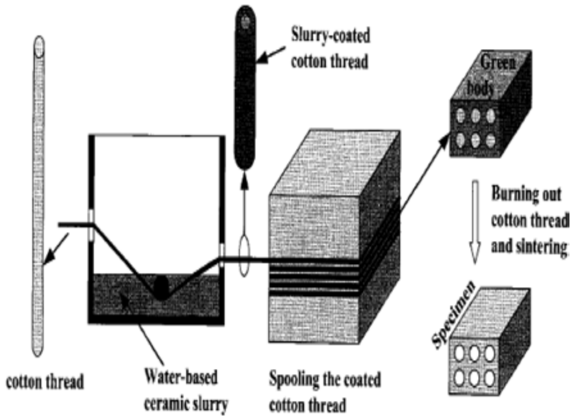


Fig. 4. Flow diagram of the fabrication of porous ceramics with unidirectionally aligned continuous pores via the slurry coating of fugitive fiber (SCF) [33].

fabrication of porous ceramics with unidirectionally aligned continuous pores via the slurry coating of fugitive fiber (SCF).

(2) Polymer blending:

Patel *et al*. [34] prepared three carbon materials having unique and precise shapes using a polymer blend technique and coating as an auxiliary technique. The polymer blend consists essentially of two kinds of polymers, i.e. a carbon precursor polymer and a decomposable polymer which disappears by pyrolysis without leaving a carbon residue. One of the carbon materials prepared is a carbon fiber including many thin pores, with diameters of sub-ìm to 1 ìm, elongated along the fiber axis.

(3) Polymer template method:

The use of core-shell structure (ceramic shell polymer core) to the template effect of the polymer template method of a porous ceramic latest technology, which uses colloidal flocculation method for producing a polymer core and core-shell ceramic shell structure, after calcination to remove polymer beads, porous structure generated. Tang *et al*. [35] fabricated well-defined porous ceramics with controllable pore size and porosity via a hetero-coagulation of template/ ceramic particle colloidal processing. Monodispersed polymer spheres were used as template and ceramic nanoparticles as inorganic building blocks to create porous structures. The preparation of well-dispersed suspensions of polymers and ceramics is essential for the fabrication of uniformly porous materials. Core-shell composites of polymer/ceramic could be obtained by mixing the oppositely charged two suspensions via electrostatic attraction following by filtration and calcination to produce macroporous ceramic materials.

In conclusion, the use of pore-forming agent method, template method and the fiber structures technology can effectively improve permeability of the ceramic membrane. These high permeability ceramic membrane preparation methods have its own applicability and uniqueness.

Table 1. the commonly used method of reduction of the maximum sintering temperature.

No.	Substance	Type	Sintering temperature / ºC
1	α-Al_2O_3		1750
2	Kaolin, feldspar	Additive	1200-1400
3	Titania, zirconia	Additive	1200-1400
4	Nano-aluminum hydroxide	Additive	1350
5	Kaolin plus 1% to 5% of the vanadium	Changebale base	700
6	Natural zeolite	Changebale base	900-1100

Researches on low Cost Ceramic Membrane Preparation Technology

Preparation of ceramic membrane support base choice

At present, the industrialization of the ceramic membrane supports the main choice of high-purity Al_2O_3 as the base material. The ridge of the powder material such as Al_2O_3, so the need to add a binder, a pore-forming agent, plasticizers and other additives can be formulated into the mud, and then molded by a certain molding method, drying and sintering the support to be made. Al_2O_3 to high cost, the manufacturing cost of Al_2O_3 ceramic membrane account for a large proportion, on the other hand, high sintering temperature, increased processing costs. Use readily available, low-cost ceramic membrane materials are to reduce manufacturing cost effective way [36-42].

Reducing the maximum sintering temperature and the cost

Maximum sintering temperature is ceramic membrane manufacturing cost is another important indicator, the higher the sintering temperature on the stove design put forward higher requirements, stoves complex structure, furnace energy consumption, production cost is high. Reduce the sintering temperature will help reduce the cost of ceramic membranes. Table 1 lists the commonly used method of reduction of the maximum sintering temperature.

In summary, low cost ceramic membrane preparation technology is primarily based on the use of ceramic membrane preparation inexpensive raw materials, optimized by the addition of sintering aids and sintering conditions and other aspects to consider, in order to promote large-scale industrial application of ceramic membranes to lay a good foundation, but in acid and alkali and other harsh environmental applications stability still need more in-depth investigation.

Conclusions

Preparation of porous ceramic membrane ceramic membrane technology research is oriented to improve the overall performance. With the development of science and technology, the porous ceramics have become increasingly demanding, in order to obtain a wider range of porous ceramic applications, from material preparation point of view, the future should be in the following areas deep research: (l) strengthening discipline a crossover study, the development can be precisely controlled pore structure and pore size distribution or a porous structure having a specific orientation of the preparation process; (2) strength and further study the relationship between porosity; (3) development of functional porous ceramic such as sound, light and other sensors porous ceramics; (4) development of environmentally friendly preparation process; (5) high porosity and high temperature high pressure nanopores developed porous ceramics is also an important research direction. In addition, the process of using porous ceramic reproduction problems should also be taken seriously enough.

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