Highly permeable supported γ-alumina membranes for water purification

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Abstract

Nanofiltration with inorganic meso-porous membranes is being considered more and more for water purification applications. For specific applications inorganic membranes may have advantages over organic polymer-based membranes due to their rigid pore structure, and thermochemical stability. However, the permeability and, partly through that, the permselectivity of inorganic membranes need to be improved before they can really become competitive. To achieve that, the membrane structure and its synthesis must be optimized and developed further to meet challenging membrane design requirements. This work shows how these requirements can be met in the synthesis of thin homogeneous supported meso-porous γ-alumina membranes on top of a hybrid α-Al_2O_3 support. Initial water permeation and permselectivity testing of these membranes gave promising results and perspectives of further improvement.

Introduction

Supported γ-alumina membranes show potential for water desalination and water softening. They offer the possibility of elevated pressure gradients, high fluxes and harsh cleaning conditions. Their selectivity rests upon the presence of space charge in the membrane meso-pores, induced by selective adsorption of ions on the γ-alumina surface [1]. State of the art membranes are made by dipping supports in a Boehmite precursor dispersion, followed by calcination at 600ºC. This results in a typical pore size of 4 nm. The precursor dispersion is made by hydrolysis-precipitation of aluminium-tri-sec-butoxide, followed by peptization with HNO_3 at $p_H = 3$. Smooth quasi-homogeneous porous supports are prepared by colloidal filtration of a dispersion of commercial 400 nm Ø α-Al_2O_3 particles, followed by sintering at 950ºC. This results in optimum dispersion and colloidal stability, and hence formation of a homogeneous support structure and a smooth surface that enables deposition of very thin membranes. All processing occurs at class 100 clean room conditions to avoid meso-defects [2].

A pure water permeability ($k_{P,m} = 1.6 \ldots 2.3 \times 10^{-20}\ m^2$) was reported for a 1.5 μm thick membrane after correction for the support [1]. Retentions of 95% and 80% were found at volume flux of $2\times10^{-5} m^3/(m^2 s)$ for 1 mole/m^3 aqueous solutions of $CaCl_2$ and NaCl, respectively at p_H=4.6. Experimental retention values were in agreement with theoretical predictions by irreversible thermodynamics involving a charge-regulation description of the equilibrium state [1]. No osmotic pressure effects are found due to the convective and the largely non-equilibrium nature of the separation process. In addition, retention is predicted to improve to near 100% at larger water fluxes, in the absence of external mass transfer effects and membrane defects.

The permeability of the 2 mm thick supports used in [1] was $k_{P,u} = 11 \ldots 16\times10^{-17}\ m^2$. Therefore, the supported membrane flux at Δp = 400 KPa will be approximately 3.7×10^{-6} $m^3/(m^2s)$. The actual membrane permeability, corrected for support resistance, offers perspectives on energy-efficient water purification and desalination, provided the following challenges can be addressed:

- Realizing much thinner membrane structures.
- Realizing equally strong but much more permeable supports.
- Minimizing effects of mass-transfer limitations at the membrane feed side.
- Improved control of membrane surface charging.

These challenges are taken up in close co-operation between UIUC and OSU within the framework of the NSF-Science and Technology Center WaterCAMPWS. Recent work shows the possibility of realizing 35 nm thick quasi-homogeneous γ-alumina membranes by control of precursor sol dilution and deposition rheology with a PVA thickener [2]. Theoretically a thickness of 10 nm is possible which would result in fluxes of 1.8×10^{-3} $m^3/(m^2s)$ at a pressure difference of 1 MPa, no support restrictions, and using the data from [1]. Much more permeable supports can be realized by directed assembly of very open 3D organized structures by robotic dispensing of α-Al_2O_3 dispersions with tailored thixotropic properties [3]. This provides a reduction in overall support resistance by at least a factor of ten with perspectives on further improvements. Mass-transfer effects are currently minimized by vigorous stirring to minimize the laminar boundary thickness at the membrane surface. With the foreseen high fluxes, laminar boundary layer theory will no longer apply and dedicated hydrodynamic process and module designs will need to be considered in a set up that is optimized at the unit operation level at least. Surface charge tuning will be addressed by using other membrane materials and application of external voltages.

Experimental studies

Quasi-homogeneous α-Al_2O_3 supports

α-Al_2O_3 powder [AKP30, Sumitomo] was mixed with an aqueous solution of nitric acid at various concentrations and dispersed with an ultrasound probe [Model 102C, Branson]. The dispersion temperature was maintained below 25ºC with a homemade cooling beaker. Partially dry disk-shaped α-Al_2O_3 compacts were made as a filter cake by vacuum filtration for 3 hours. The compacts were sintered in air with a heating/cooling rate of 2ºC/min and 10 hrs soak time at temperatures ranging from 650-1200ºC.

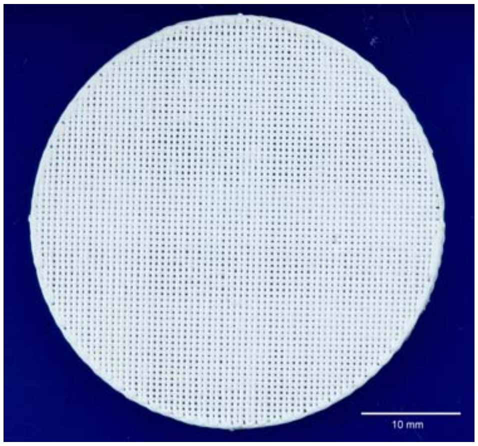

Figure 1: Robocast 3D support.

The apparent bulk densities of the supports were measured with a modified mercury pycnometer [Model number DBA100-1, PMI, USA] to determine the optimized nitric acid concentration for support preparation. The morphology of polished and unpolished surfaces were directly observed in Focused Ion Beam (FIB) cross-sections with SEM/TEM.

High permeability – high strength 3D organized α-Al_2O_3 support structures, as shown in figure**Error! Reference source not found.** were made by robocasting [3] a thixotropic ink, similar to the dispersions used for quasi-homogenous α-Al_2O_3 supports. The thixotropic properties were realized by using an electrosteric (PEI) stabilizer instead of the HNO_3, and gelling by increasing the p_H from, initially, 9. This ink is fluid at high (forced) shear stress conditions in the dispensing needle but immediately solidifies at low (natural gravitation) shear stress in the assembly. After rigidizing the 3D structure by sintering, a capping top layer was deposited on it by a process similar to that described for the quasi-homogeneous α-Al_2O_3 supports. A cross section of the interface between the capping layer and the robocast 3D support is shown in figure 2. The average thickness of the capping layer is estimated to be less than 0.2 mm, which dramatically increases the apparent permeability of the whole supported membrane structure.

γ-alumina membrane

The γ-alumina membranes were made by dipping supports in a nano-particle precursor dispersion, followed by calcination at 600ºC. The precursor dispersion was made by hydrolysis-precipitation of aluminium-tri-sec-butoxide followed by peptization with HNO_3 at $p_H = 3$, and removal of larger particles and agglomerates by filtration and centrifugation. The thus prepared sol was diluted 20× with 3 wt% polyvinyl alcohol (PVA) in $p_H = 3.5$ HNO_3 solution. Addition of PVA increases the viscosity of the sol and promotes membrane formation during dip-coating. A detailed description of preparation and characterization of the membrane is presented in [2].

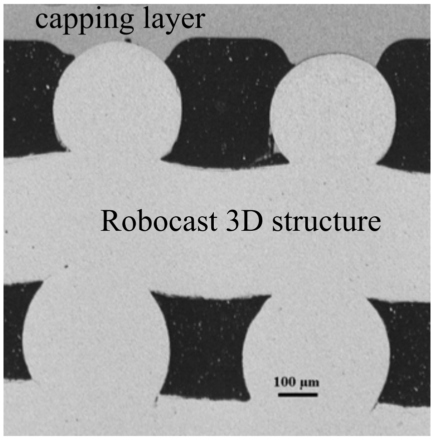

Figure 2: Cross section of α-Al_2O_3 3D periodic structure and the α-Al_2O_3 capping layer.

Water permeation and purification

A dead-end cross-flow pressure chamber has been constructed for water permeation and purification experiments. Special attention has been paid to the O-ring sealing configuration to avoid shear strain in the meso-porous layer. Permeates are collected separately for the “perpendicular” flow and the “spreading” flow through the supported membrane edge. An autoclave stirrer is installed just above the membrane surface to minimize mass-transfer limitations in the feed. Temperature, pressure and stirring parameters at the feed side are fully monitored with a computer. Water purification is tested with NaCl, $CaCl_2$ solutions and artificial sea water.

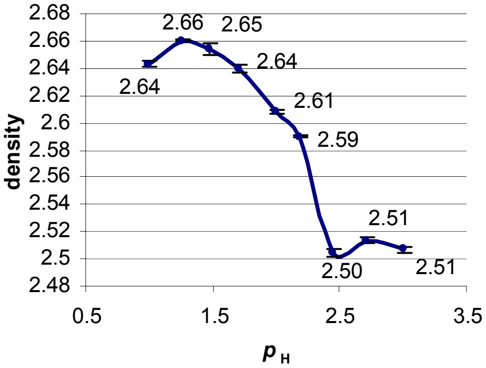

Figure 3: Dispersion p_H vs apparent bulk density of quasi-homogeneous colloidal filtration support.

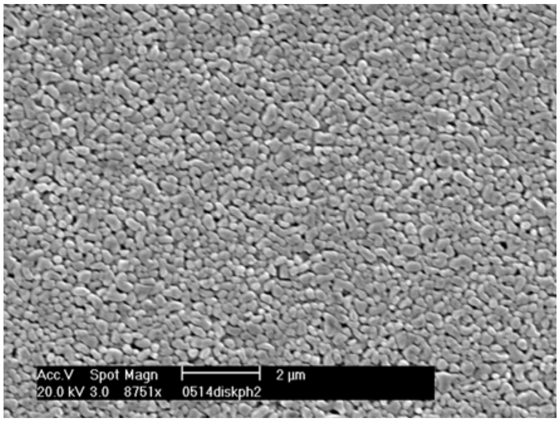

Figure 4: Optimized support surface.

Results and discussion

Quasi-homogeneous support characterization

The apparent support structure density is an important macroscopic indication for essential porous material properties, such as particle packing, porosity and strength. For this work, a mercury pycnometer was modified to provide sufficiently accurate densities ($\pm 0.01 g/cm^3$) for supports prepared under different conditions, such as dispersant p_H, see figure 3. The optimum

$p_H = 2$ appears to a compromise between a high compact density due to colloidal stability and due to dissolution-re-precipitating of alumina material. The optimized dispersion concentration of $p_H = 2$ is also confirmed with direct SEM observation as shown in figure 4. The homogenous random packing structure provides an optically smooth surface, which is favorable for the thin membrane layer deposition.

γ-alumina membrane characterization

Large agglomerates are eliminated from the precursor sol by filtration on 0.8, 0.45, and 0.22 μm Ø filters and centrifugation for 1 hour at 50,000g. Sol characterization during these treatments is done by dynamic laser scattering (DLS) [BI-9000AT, Brookhaven], see figure 5. γ-alumina membranes prepared with purified sol showed a dramatic improvements in homogeneity and adhesion, essential for membrane performance. A 35 nm thin layer was synthesized by using a diluted sol with PVA addition, see figure 6.

Water permeation and purification

Water permeation tests were conducted to characterize the permeability and strength of supports and supported membranes. It is found that the strength increases with increasing sintering temperature, as expected. However, the permeability reaches a maximum value of 3.71×10^{17} m^2 at a sintering temperature of 950ºC, see figure 7. It is believed that coarsening in combination with little shrinkage is responsible for the permeability increase. During initial stage sintering, the average pore size increases as smaller particles are consumed by larger particles. When the sintering temperature increases above 950ºC, supports undergo significant shrinkage and the pores eventually close.

The flux in a γ-alumina membrane on a quasi-homogeneous α-Al_2O_3 support is measured in the same way and a corrected permeability of 7.7×10^{-20} m^2 was found, as calculated with a series permeation model. This result compares favorably with the state of the art value of ~2×10^{-20} m^2, but requires more detailed analysis of the supported membranes morphology. Hybrid membrane supports, consisting of a robocast 3D periodic α-Al_2O_3 structure and a ~0.2 mm quasi-homogeneous α-Al_2O_3 capping layer, show a very promising permeability of 5×10^{-15} m^2. Commercial supported organic membrane processes show a water flux of ~10^{-5} m^3/(m^{2}s) at Δp = 1 MPa. If the ideal 10 nm γ-alumina layer is realized on a virtually non-resistive but strong support, a flux of ~10^{-2} m^3/(m^{2}s) flux can be achieved at similar conditions but these membranes will also allow for much higher pressures and likewise fluxes and permselectivities.

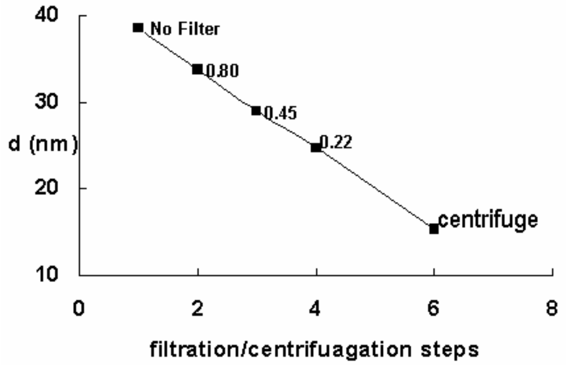

Figure 5: DLS sol particle size during purification steps. The numbers indicate the filter pore Ø.

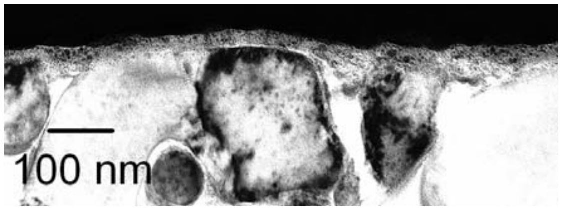

Figure 6: TEM image of an FIB cross section of a thin γ-alumina membrane on an α-Al_2O_3 support.

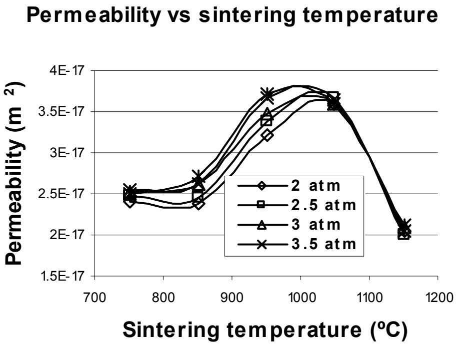

Figure 7: Quasi-homogeneous support permeability vs sintering temperature at various Δp.

The permselectivity of the membranes was demonstrated in purification experiments with aqueous solutions of 10^{-3} mol/L $CaCl_2$, 10^{-3} mol/L NaCl and artificial sea water. The purification experiments of the membranes show encouraging results, summarized in table 1. The p_H value of the $CaCl_2$ and NaCl solution is adjusted with HCl to 4.6 because in that case the γ-alumina membrane surface is properly charged with adsorbed positive ions and not chemically attacked. The sea water p_H value was not adjusted. The applied pressure was 300 kPa and the stirrer rotation speed 1500 RPM. p_H measurements and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analyses were carried out for the $CaCl_2$ and NaCl solutions after the permeation experiment. A higher rejection rate for Ca^{2+} than Na^+ is due to the higher valence of Ca^{2+} ions and possibly preferential adsorption of Ca^{2+} ions on the γ-alumina surface. An obvious trend of p_H neutralization in the permeate was observed for all the experiments.

Table 1: Purification results of γ-alumina membranes on quasi-homogeneous α-supports.

$CaCl_2$	p_H	Ca^{2+} ppm	NaCl	p_H	Na^+ ppm	Sea water	p_H	Conductivity 10^{-3} s/cm
Original	4.8	39.29079	Original	4.5	22.0	Original	8.3	5.31
Retentate	4.9	39.67523	Retentate	4.5	22.9	Retentate	8.3	5.38
Permeate	6.7	0.48831	Permeate	6.5	4.8	Permeate	7.9	5.04
Rejection		98.7%	Rejection		79.0%	Rejection		6.3%

The meso-porous γ-alumina membranes show typical nanofiltration behavior, in which retained hydrated ions (Ø ~0.5 nm) are much smaller than the membrane pore size (~4 nm). The surface adsorption chemistry and electrokinetic interaction between the adsorbed ions and the ions in the solution play a key role in this behavior. A net surface charge density will develop spontaneously when the membrane is immersed in the aqueous electrolyte solution, which causes a potential difference between the solution and the internal membrane phase. This potential difference is referred as Donnan potential. It prevents free diffusion/convection of positive and negative ions between the solution and the membrane phase.

Conclusions

Supported meso-porous inorganic membranes show potential for rugged water purification applications, provided the permeability and the permselectivity are fully optimized by optimizing the supported membrane structure. Very high water fluxes are possibly achieved in such membranes due to the convective transport mechanism. Membrane pore dimensions and surface chemistry need to be further optimized to improve permselectivity for several applications. A 3 layer hybrid membrane support structure of meso-porous γ-alumina on quasi-homogeneous α-Al_2O_3 on 3D periodic open α-Al_2O_3 might be an important step in realizing interesting combinations of permeability and permselectivity.

Future work will focus on the following:

- Optimization of the 3 layer structure with a 10 nm γ-alumina thickness, a 10 μm quasi-homogeneous α-Al_2O_3 thickness, and a 2 mm 3D periodic α-Al_2O_3 thickness.
- New meso-porous layer materials with better chemical stability and improved surface characteristics.
- Membrane structures that allow for surface charging by an external applied potential as shown in [4].

Acknowledgements

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