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Ultra-Stable Inorganic Meso-Porous Membranes for Water Purification

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Abstract: Thin supported inorganic mesoporous membranes are used for removal of salts, small molecules (PFAS, dyes, polyanions) and particulate species (oil droplets) from aqueous sources with high flux and selectivity. Nano-filtration membranes can reject simple salts with 80-100% selectivity through a space charge mechanism. Rejection by size selectivity can be near 100% since the membranes can have a very narrow size distribution. Mesoporous membranes have received particular interest due to their (potential) stability at operational conditions and defouling operations. More recently membranes with extreme stability became interesting with the advent of in-situ fouling mitigation by means of ultrasound, emitted from within the membrane structure. For this reason we explored the stability of available and new membranes with accelerated lifetime tests in aqueous solutions at various temperatures and pH values. Of the available ceria, titania, magnetite membranes none were actually stable at all test conditions. In earlier work, it was already established that meso-porous alumina membranes have very poor stability. A new nano-filtration membrane was made of cubic zirconia membranes that exhibited a near perfect stability. A new ultra-filtration membrane was made of amorphous silica that was fully stable in ultrapure water at 80°C. This work provides details of membrane synthesis, stability characterization and actual stability data.

Keywords: inorganic membranes; nanofiltration; ultrafiltration; water purification

1. Introduction

Thin supported mesoporous inorganic membranes are used in water purification and as intermediate layers to deposit other membranes. They typically consist of oxides such as Al_2O_3, CeO_2, SiO_2, TiO_2, and ZrO_2. Their porosity is around 35%, their pore size between 2 and 50 nm and their thickness between 10 nm and 10 μm [2–5]. The membranes are generally present (supported) on thick, permeable macro-porous supports [6]. The ultimate liquid transport performance that can be obtained is

$f_\ell = 4.4\times10^{-12}$ [m] and $f_V = 1600$ [L/(m²Bar·h)] for a nano-filtration membrane with a porosity of 35%, straight 2 nm pores and a thickness of 10 nm.

$f_\ell = 2.2\times10^{-11}$ [m] and $f_V = 7900$ [L/(m²Bar·h)] for an ultra-filtration membrane with a porosity of 35%, straight 10 nm pores and a thickness of 50 nm.

$f_\ell = j_V \times \eta_\ell / \Delta p$ is the mechanical permeance, $f_V = j_V / \Delta p$ the volumetric permeance, j_V is the volumetric flux, η_ℓ the liquid viscosity and Δp the mechanical pressure difference. For the calculation of f_V a dynamic viscosity of 10^{-3} [Pa·s] is assumed. The underlying assumptions in the calculation of f_ℓ and f_V are incompressible non-slip (laminar) flow, following the Hagen-Poiseuille equation, absence of support resistance and a minimum thickness that is 5× the pore diameter. The f_V of known polymeric nanofiltration membranes ranges from 0.3 to 1.6 L/(m^2Bar·h) [7–9]; f_V of known organic ultrafiltration membranes is <500 L/(m^2Bar·h) [10–13]. This marked difference is associated with a higher porosity and smaller minimum thickness of the inorganic membranes. However, the ultimate values for supported inorganic membranes have not yet been attained. In a recent study of supported ceria membranes with 3 nm pores f_V = 43 L/(m^2·h·bar) and >80% Na+ rejection were obtained for a thickness of 200 nm. Further increases of f_V would require more permeable support structures and more development of thin membrane deposition processes.

By far the most well-known supported meso-porous inorganic membrane is γ-alumina, developed during the Manhattan project for the enrichment of ^{235}U since 1939 [26]. Work on γ-alumina membranes for other applications started in the 1980s [27–29]. T.A. Kuzniatsova et al. presented methods to further improve the microstructural homogeneity of γ-alumina membranes. M.C. Schillo et al. reported on γ-alumina membranes by means of rapid thermal processing with near 100% rejection of Ca^{2+} ions [30]. The use of meso-porous titania and zirconia membranes for large scale industrial and environmental water purification has been widely published [31–34]. In addition, the possibility was studied of further improvements by making composite structures. Zhu et al. reported a mullite-carbon nanotube (CNT) composite membrane with an average porosity of 56% and a long-term permeance up to 38.7 L/(m^2Bar·h). They concluded that the addition of CNTs resulted in a stable, highly porous network and hence high permeability [35]. CNTs consist of pure carbon and hence can be considered as fully water stable at normal conditions. In [35] no data were reported for the water stability of the mullite phase. More recently the water purification properties were studied of thin supported graphene oxide (GO) membranes [36,37]. Like what is the case for CNTs the GO can be considered fully water stable. But since thin CNT and GO membranes require oxidic supports and/or additives, the question of the water stability of oxide membranes remains.

The mesoporous oxides can consist of a single or multiple phases, be amorphous or crystalline and contain cationic mixtures such as in $(Ti,Zr)O_2$ and $(Y,Zr)O_{2-\delta}$. They can also contain substantial amounts of protons and hydroxide groups and for this reason we prefer to indicate γ-Al_2O_3 as γ-alumina. An advantage of mesoporous inorganic membranes over their polymeric counterparts is the stability of the porous structure at high pressures, absence of swelling in pretty much any solution and, presumed, chemical resistance under harsh conditions [14–16]. In addition, mesoporous inorganic membranes can be applied on, also inorganic, piezo-electric macro-porous supports that can generate ultrasound by application of an alternating voltage during operation [17–19]. The ultra-sound then breaks up laminar boundary layers and keeps the surface clean. Mao et al. [18] investigated the anti-fouling performance of a composite membrane containing a CNTs/alumina top layer and a piezoelectric $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) support. They found that with the application of an alternating voltage of 20 V at a frequency of 190 kHz, the poled membrane was chemically stable in a 2.5g/L dextran solution for hours and had a permeance of 55.6 L/(m^2Bar·h) at room temperature. Non-piezoelectric supports can be brought in ultrasonic resonance by application of external piezo-electric transducers. In any case the supports must have a simple (tubular) geometry with dimensional tolerances within microns, only possible with inorganic structures.

While supported inorganic membranes are and will remain more expensive than polymeric membranes, the advantages as mentioned may justify the higher cost.

An important requirement for practical application of the membranes is operational stability which includes resistance to contamination (fouling), ageing, reactions with the filtration medium and cleaning operations. While is it known that γ-alumina is not stable in aqueous solutions at any pH and even ambient conditions, the other oxides are generally assumed to be fully stable in aqueous environments with pH values around 7 [20–22]. But their actual stability over longer times, elevated temperatures and more extreme pH values is mostly unknown. Hence a proper up-front analysis of the stability of water filtration membranes is needed, in particular for long term water filtration, high temperature membrane reactors, and membrane distillation. Hence we decided to develop a method for accurate and precise determination of the actual long term solution stability of mesoporous inorganic membranes.

As will be elaborated in the methods and experiments section, the options for usable stability studies are limited to a direct observation of membrane thickness and density by a non-destructive and preferably non-contact method. To obtain meaningful results the membrane microstructure must be very well defined, reproducible between samples with little variation over the membrane surface. In [39] we introduced and used spectroscopic ellipsometry (SE) as a non-destructive, non-contact method to determine membrane thickness and porosity. Samples as indicated have become available through deposition of homogeneous nano-particle dispersions on optically smooth macro-porous supports followed by thermal processing [5,40–44].

We anticipated that by using SE with the samples as indicated we would be able to resolve very slow dissolution and densification of supported meso-porous membrane material. To demonstrate the use of this method, we made membranes as indicated with, presumed, stable compositions and exposed them to water and dilute aqueous solutions at temperatures up to 80°C for up to 6 weeks. We characterized these membranes with SE at intervals to obtain significant changes.

In the work presented we used membranes, consisting of TiO_2 anatase made through a alkoxide hydrolysis method, (cubic) CeO_2, yttria-stabilized zirconia (YSZ) and Fe_3O_4 (magnetite) made through sonochemical precipitation, and amorphous SiO_2 made from a commercially available dispersion (Ludox AS, obtained from Sigma-Aldrich). Homogeneous dispersions of precursors for those oxides were adjusted for deposition properties by adding polyvinyl alcohol (PVA). Subsequently, thin particle layers were formed on smooth macro-porous supports by dip-coating. The eventual membrane composition was formed by drying and rapid thermal processing (RTP) with target temperatures of 600 to 700°C. For the exposure experiments we used mostly ultra-pure water and occasionally a targeted adjustment of the pH by adding nitric acid (HNO_3) or tetramethylammonium hydroxide (TMAOH).

2. Materials and Methods

Thin supported inorganic membranes are generally made by deposition of a stable precursol sol on macro-porous α-Al_2O_3 supports, followed by thermal processing [6]. The deposition occurs by film coating and/or slip-casting (filtration driven by capillary suction). The sols are made by wet-chemical precipitation or polymerization methods in which well-dispersed particles are obtained, either immediately or by peptization [5,23,24]. A post-treatment of the sols to remove larger particles and agglomerates is generally needed. In addition, molecular or polymeric compounds are added to promote membrane formation. Thermal processing consists of drying, removal of additives, conversion of precursor phases into the target structure and partial sintering to form a coherent structure. During sintering, particles in a compact form necks and merge, driven by surface tension reduction. At least some neck formation (with little shrinkage) is needed to give the structure sufficient strength. [25].

The overall membrane synthesis process used for the studies, presented here, includes five steps. 1) macro-porous α-alumina supports are prepared by a colloidal casting method. 2) precursor dispersions containing nanosized particles are synthesized by alkoxide hydrolysis or sonochemical precipitation methods. 3) supported membrane precursors are made by dip-coating mixtures of precursor dispersions and additives such as binder and lubricant (PVA) and defoamer (ethanol) on α-Al_2O_3 supports. 4) most of the water and some additives are removed by drying in an oven. 5) the final oxide structure is obtained with rapid thermal processing (RTP).

2.1. Support synthesis

Macro-porous α-alumina supports with an optically smooth deposition surface were made according to a procedure as described in [6]. Stable dispersions of 50 wt% α-Al_2O_3 powder (AKP30, Sumitomo Chemical, Japan) in 0.01M aqueous HNO_3 (Sigma Aldrich, USA) were prepared by ultrasonification (Branson, USA), followed by mesh screening (20 μm), removal of microbubbles with biaxial centrifugation (Thinky, USA) and vacuum filtration. After drying in the filtration mold for ~24 hours, the disk-shaped consolidates were transferred into an alumina crucible boat (Fisher Scientific, USA) and sintered at 950°C for 10 hours using heating and cooling rates of 2°C/min. Thus obtained α-Al_2O_3 disks had a diameter of 42 mm, a thickness of about 2 mm, and a porosity of 35% and bulk pore size of 100 nm as determined by mercury porosimetry (Micromeritics, USA).

2.2. Nanoparticle dispersion syntheses

2.2.1. Titania dispersion synthesis

The titania dispersion was made starting from hydrolysis of titanium (IV) isoproproxide. Ultrapure de-ionized (DI) water (0.056 μS/cm; Millipore, USA) was combined with HNO_3 in a 40:1 molar ratio. While the solution was stirred at 50ºC, a mixture of Titanium (IV) isopropoxide (Acros Organics, USA) and isopropanol (Fisher Scientific, USA) was added via a syringe and syringe pump at a rate of 150 mL/hr. The use of a syringe prevented air exposure of the alkoxide. The titania dispersion, thus obtained, was centrifuged at 25,000 rpm for 3 hrs (Allegra 64R; Beckman Coulter, USA). Immediately after centrifugation, 10 mL of the supernatant was stored for use in membrane deposition.

2.2.2. Sonochemical precipitation

Homogeneous ceria precursor dispersions were synthesized in four steps: 1) a solution of cerium ammonium nitrate ($(NH_4)_2Ce(NO_3)_6$, (Sigma Aldrich, USA) was treated with intense ultrasound waves, generated with an ultrasonic probe operating at 20 kHz and 20…35 W. Micro-bubbles formed in the tensile phase of the ultrasound collapse quickly in the compression phase, causing local temperatures of up to 5000K. This results in the formation of isolated and insoluble nuclei at the vanishing points of the bubbles. 2) TMAOH (Sachem, USA) was added to form larger particles from the nuclei by precipitation. 3) N,N-Bis(2-hydroxyethyl) glycine (Bicine, Sigma Aldrich, USA) was added to suppress the agglomeration, which would adversely affect subsequent processing. Due to the nature of this process the nanoparticles do not agglomerate and have a narrow size distribution with in a range of 10 nm. 4) After sonication, dialysis was performed to remove excess ions, in turn to avoid precipitation of salts in later processing and to further improve dispersion stability. An aqueous solution of 1 N HNO_3 (Sigma Aldrich, USA) with a pH of 2 was used as dialysate.

YSZ and magnetite nano-particle precursor dispersions were also prepared by similar sonochemical precipitation methods. For the YSZ synthesis, an aqueous solution of yttrium nitrate hexahydrate ($Y(NO_3)_3{\cdot}6H_2O$, Sigma Aldrich, USA) and zirconium oxynitrate hydrate ($ZrO(NO_3)_2{\cdot}xH_2O$, Sigma Aldrich, USA) was used as a precursor in step 1). A Magnetite dispersion was made by using an aqueous iron nitrate (3-hydrate) solution in step 1.

2.3. Dynamic light scattering

The particle size distributions of the synthesized nano-particle dispersions were measured using Dynamic Laser Scattering (DLS, Malvern Instruments, UK). In DLS diffusion coefficients of Brownian motion are obtained which, in turn, are used to obtain particle size distributions from the Stokes-Einstein equation [47].

2.4. Stability analysis

The stability of inorganic meso-porous membranes can be studied by observation of micro-structural changes, changes in transport properties and by analysis of trace ions in solutions that have been in contact with the membrane material. However, as will be shown in this study, dissolution rates of "stable' membranes can be as small as 1 nm over 8 weeks ($2{\times}10^{-16}$ [m/s]). At such low dissolution rates any changes cannot be observed with normal, destructive, microstructure characterization. In transport characterizations the membrane has to be kept in the module to obtain sufficient reproducibility. But even clean water characterizations are dominated by residual fouling by module components while no clear distinction can be made between thickness and pore size effects. A dissolution rate of 2×10^{-16} [m/s] for TiO_2, a membrane surface of 1.4×10^{-3} [m^2] as we use, and a water volume of 1 L would cause a Ti^{4+} concentration change of 7×10^{-8} [mol/L]. While this is close to the ICP-OES detection limit of 10^{-7} [mol/L] and above the ICP-MS detection limit of 2×10^{-9} [mol/L], contamination from the ambient and liquid, initially and over time are likely to exceed those values by orders of magnitude [38]. In addition, analysis of the liquid is still an indirect method.

Spectroscopic ellipsometry

In spectroscopic ellipsometry (SE) the changes in polarization of light, reflected from a sample surface is analyzed to obtain properties of single- and multi-layer structures such as thickness, refractive index, optical absorption, and anisotropy of and gradients in such properties [48]. Ellipsometry measurements can also be done in-situ to monitor membrane formation and adsorption [49,50]. The change in polarization after reflection is expressed in terms of the intensity, r_s, of light with polarization perpendicular to the incidence plane and the intensity, r_p, with polarization parallel to the incidence plane. Measured values of r_p and r_s are then used to obtain Ψ and Δ in

$$\tan(\Psi)\exp(i\Delta) = r_p / r_s \qquad (1)$$

where tan(Ψ) is the amplitude ratio between reflected light with p- and s-polarizations and Δ the phase difference between reflected light with p- and s-polarizations [51]. SE measurements were performed for every sample before and after each stability test using a VASE ellipsometer (J.A. Woollam, USA) in which Ψ and Δ were obtained for three incident angles, 65, 70 and 75° in the wavelength range of 300 to 1500 nm. Prior to the experiment, the samples were marked such that the data were always obtained for the same location.

The SE data were analyzed with J.A. Woollam's WVASE software. Since the membranes were mostly transparent and colorless at the wavelengths of observation, the Cauchy model was used for the wavelength dependence of the refractive index.

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \qquad (2)$$

where n is the refractive index, λ is the wavelength, and A, B, and C adjustable parameters. Best fits were obtained by minimization of the non-linear Mean Square Error [51]. Precisions estimated were obtained assuming a normal distribution with a 95% confidence interval.

The following effective characteristics were obtained, going from the membrane surface into the support

A roughness of the exposed membrane surface, being typically within 1 nm.

A membrane thickness in the range of 10 nm and 1 μm with a precision and variation of the membrane surface of ±1 nm.

An effective thickness of intermixing between the membrane and the support on the order of 50 nm for supports with a surface pore size of ~40 nm and a short range surface roughness of ~25 nm [6,45,46].

A refractive index of 1.5 to 2±0.05 that can be used for an accurate estimate of the porosity through the Bruggeman method [39].

3. Results and discussion

All nano-particle dispersions appeared visually transparent. The titania dispersion made by alkoxide hydrolysis and centrifugation had a particle size distribution of 1 to 4 nm with an average of 2.3 nm. The sonochemical precipitation syntheses resulted in precursor dispersions with size distribution of 2 to 3.5 nm with an average size of 2.8 nm for YSZ, and 4 to 8 nm with an average of 4.2 nm for ceria. The as-received silica dispersion (Ludox AS) had a particle size distribution of 4 to 6.4 nm with an average of 5.2 nm. The membranes, made with these dispersions had a thickness of 100 to 300 nm and showed opalescent effects that are characteristic for thin homogeneous transparent membranes. The titania, zirconia, ceria, magnetite, and silica membranes appeared light blue, light yellow, orange, dark brown and colorless, respectively. No delamination from the supports or micron-scale roughness was observed.

The results of the stability characterizations are presented in Tables 1–4.

Table 1. Results of stability measurements for ceria membranes.

	In 80°C DI		In 60°C DI		In 60°C HNO_3	
Week	***X* [nm]**	***n***	***X* [nm]**	***n***	***X* [nm]**	***n***
0	191.2±1.8	1.893±0.001	191.7±2.6	2.000±0.001	189.0±1.3	1.990±0.001
1	190.2±2.3	1.853±0.001	192.1±3.1	2.000±0.001	190.7±3.7	2.000±0.001
2	190.6±1.5	1.852±0.001	188.9±1.7	2.017±0.001	191.0±1.8	1.953±0.001
3	187.8±2.1	1.897±0.001	191.3±2.3	2.001±0.001	188.2±2.0	1.977±0.001
4	149.6±2.7	2.040±0.002	193.7±3.7	2.003±0.001	179.8±3.2	1.995±0.001
5	134.1±3.0	2.021±0.001	192.3±3.0	1.999±0.001	175.3±4.7	2.000±0.001
6	135.3±3.3	2.020±0.001	194.0±5.8	2.000±0.001	170.5±4.3	2.013±0.002

Table 2. Results of stability measurements for titania, YSZ and amorphous silica membranes in 80°C DI.

	TiO_2		YSZ		SiO_2	
Week	***X* [nm]**	***n***	***X* [nm]**	***n***	***X* [nm]**	***n***
0	177.0±2.1	1.363±0.001	256.3±3.3	1.866±0.001	177.8±2.3	1.179±0.001
1	176.1±2.0	1.362±0.001	259.9±4.8	1.853±0.001	177.7±3.9	1.181±0.001
2	176.0±2.1	1.362±0.001	256.0±5.0	1.847±0.001	177.8±2.5	1.181±0.001
3	166.3±3.5	1.370±0.001	255.1±3.8	1.849±0.001	177.8±2.1	1.181±0.001
4	168.7±4.7	1.370±0.002	249.7±8.1	1.831±0.001	177.6±2.5	1.193±0.001
5	166.2±2.0	1.361±0.001	249.9±8.7	1.830±0.002	177.8±3.1	1.181±0.001
6	166.2±2.5	1.359±0.001	249.7±3.0	1.830±0.001	177.8±3.7	1.181±0.001

Table 3. Results of 24-hr stability measurements for magnetite membranes.

Solution and pH	Before *X* (nm)	After *X* (nm)	Before *n*	After n
TMAOH @ 11	258.3±3.9	253.7±5.3	4.623±0.001	5.147±0.001
HNO3 @ 5	253.7±5.3	265.1±4.6	5.147±0.001	3.785±0.001
HNO3 @ 4	265.1±4.6	216.6±7.5	3.785±0.001	6.834±0.002
HNO3 @ 3	216.6±7.5	197.3±8.3	6.834±0.002	6.346±0.002

Table 4. Membrane dissolution and densification rates calculated from measurements.

Membrane	Condition	Dissolution rate (nm/week)	Densification rate (%/week)
CeO_2	In 80°C DI	11.5±1.3	4.6±0.05
	In 60°C DI	0.0±0.4	0.0±0.02
	In 60°C at pH=2	3.4±0.7	1.1±0.03
TiO_2	In 80°C DI	2.1±0.5	0.0±0.02
YSZ	In 80°C DI	1.6±0.4	-0.4±0.02
SiO_2	In 80°C DI	0.0±0.0	0.1±0.00

It was found that the variation in thickness of the membrane across the membrane surface within a radius of 1.5 mm was typically 1 nm. The difference in membrane thickness between samples, made in a similar way was within 10 nm. Analysis of the stability data indicated that the dissolution rate could be resolved within 0.1 nm/week and the densification rate within 0.1%/week.

Except for amorphous silica and YSZ none of the other oxides appeared to be fully water-stable at 80°C within the limitations of observation. Below is a summary of findings thus far, including literature results for γ-alumina

Meso-porous γ-alumina made through peptization of hydrolyzed aluminum-tri-sec-butoxide (ATSB) typically dissolves in aqueous solutions of any pH within 24 hrs [20–22]. One way to suppress this is to add substantial Al^{3+} ions to the solution [21].

Meso-porous amorphous SiO_2 made from Ludox AS dispersions appeared to be fully stable, within the limits of observation, in ultrapure water at temperatures of 80°C.

Crystalline CeO_2 membranes made through sonochemical precipitation were stable in ultrapure water at 60°C but at 80°C their thickness decreased at a rate of 11.5 nm/week while they densified at a rate of 4.6%/week. The membranes dissolved at a rate of 3.4 nm/week and densified at a rate of 1.1%/week in 0.01M aqueous HNO_3 at 60°C.

Cubic zirconia (YSZ) made through sonochemical precipitation was quite stable with a minor dissolution rate of 1.6 nm/week in ultrapure water at 80°C. Meanwhile its porosity increased at a rate of 0.4%/week during the test period, indicating that a slight dissolution at 80°C results in an increased membrane porosity. Yttria-stabilized zirconia can be unstable in water due to yttrium segregation. However this phenomenon is known to occur only at larger particles sizes of >400 nm [52] while the grain size in our membranes is ~5 nm [53,54].

Magnetite Fe_3O_4 was stable in an aqueous solution of TMAOH with pH of >11. It quickly dissolved in aqueous solutions of nitric acid with pH values of <4. This is expected since iron oxides are known to dissolve quickly at low pH.

Anatase TiO_2 made via alkoxide hydrolysis was stable in ultrapure water at 80°C for 2 weeks. Then the thickness decreased by 10 nm during week 3 but did not change from week 4 to week 6. The refractive index hardly changed (±0.01) during 6 weeks. The thickness decrease is significant and is tentatively ascribed to a transition to a more stable TiO_2 phase.

During the experiments the ultrapure water likely became CO_2-buffered due to dissolution of CO_2 from ambient air. Such a buffering leads to a pH = 6.8 at room temperature, 6.5 at 60°C and 6.2 at 80°C. In addition, some Na^+ and borate ions may have been released from the glass container. We believe that neither effect is of any significance for the water stability experiments conducted.

4. Conclusions

It was found that, that commonly used and proposed anatase titania and zirconia membranes do not have a complete stability in water at elevated temperature. This raises concerns about their actual long-term water stability at any condition. Amorphous meso-porous silica is not widely explored for water purification but appears to be much more stable. Since the intended use of meso-porous inorganic membranes is in very large scale water purifications, the results and methods provided in this work are deemed essential to make better choices for membrane compositions that are taken in development. The fact that SE can be conducted in-situ, at actual process conditions, can be beneficial to obtain the most relevant stability information with a limited time frame.

Homogeneous thin mesoporous amorphous silica, ceria, titania, YSZ and magnetite membranes could be synthesized for demonstrating the use of spectroscopic ellipsometry in water stability studies. It was possible for all these membranes to obtain the thickness and refractive index with a precision of 1 nm and 0.001, and rates of change as small as 0.1nm/week and 0.001/week, respectively. However the results may not be fully representative for any meso-porous oxide membrane with a similar composition. The total duration of the work presented has been about a year. A systematic investigation of the stability of just one oxide with the membrane made through one particular route in a range of solution compositions may take a lot more time and effort. But yet we believe that the trends in stability as shown are significant. One truly remarkable result is the combination of complete stability of amorphous silica in water up to 80°C and the factual complete instability of γ-alumina. Microporous amorphous silica membranes are well-known for their high flux, high selectivity separation of light molecules [55,56]. However these membranes are reported to be unstable in humid air of ~20% relative humidity at 100°C [57]. On the other hand the microporous amorphous silica membranes, reported thus far, are mostly made by modification of supported γ-alumina. Consequently we speculate that the instability may have been caused by degradation of the γ-alumina membrane rather than the silica modification. To our knowledge, the only other type of meso-porous scaffold is meso-porous silica made by surfactant-assisted self-organization, but no stability results have been reported for those membranes [58,59]. Hence we recommend investigation of the performance of micro-porous amorphous silica membranes with scaffolds made of amorphous silica, ceria, zirconia, titania, magnetite or other water-stable oxides.

The water-stable oxides identified in this work all have 4+ charges. Hence other interesting systems to investigate include GeO_2, SnO_2, and PbO_2. PrO_2 would be similar to CeO_2 but tends to stabilize into Pr_6O_{11} with substantial Pr^{3+} which, in turn, results in substantial solubility as we confirmed in a quick test. The observed densification behavior of ceria membranes and increase of porosity in YSZ membranes may be utilized to achieve membranes structures that cannot be otherwise obtained.

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Symbols and abbreviations

f_ℓ:	Mechanical permeance; $f_\ell = j_V \times \eta_\ell / \Delta p$.
f_V:	Volumetric permeance; $f_V = j_V / \Delta p$.
j_V:	Volumetric flux.
η_ℓ:	Liquid viscosity.
Δp:	Mechanical pressure difference.
CNT:	Carbon nanotube.
PZT:	Lead zirconate titanate ($PbZr_{0.52}Ti_{0.48}O_3$).
AKP30:	Sumitomo Chemical AKP30 α-Al_2O_3 powder.
GO:	Graphene oxide.
DI:	De-ionized.
YSZ:	Yttria-stabilized zirconia.
DLS:	Dynamic Laser Scattering.
TMAOH:	Tetramethylammonium hydroxide.
PVA:	Polyvinylalcohol.
RTP:	Rapid Thermal Processing.
SE:	Spectroscopic Ellipsometry.
r_s:	Intensity of light with polarization perpendicular to the incidence plane.
r_p:	Intensity of light with polarization parallel to the incidence plane.
tan(Ψ):	Amplitude ratio between reflected light with p- and s-polarizations.
Δ:	Phase difference between reflected light with p- and s-polarizations.
n:	Refractive index.
λ:	Wavelength.
X:	Membrane (layer) thickness.

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