

Review

## Microporous Silica Based Membranes for Desalination

Muthia Elma, Christelle Yacou, David K. Wang, Simon Smart and João C. Diniz da Costa \*

Films and Inorganic Membrane Laboratory, School of Chemical Engineering, The University of Queensland, Brisbane, Queensland 4072, Australia; E-Mails: m.elma@uq.edu.au (M.E.); c.yacou@uq.edu.au (C.Y.); d.wang1@uq.edu.au (D.K.W.); s.smart@uq.edu.au (S.S.)

\* Author to whom correspondence should be addressed; E-Mail: j.dacosta@eng.uq.edu.au; Tel.: +62-7-33656960; Fax: +62-7-33654199.

Received: 4 July 2012; in revised form: 11 August 2012 / Accepted: 21 August 2012 /

Published: 3 September 2012

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**Abstract:** This review provides a global overview of microporous silica based membranes for desalination via pervaporation with a focus on membrane synthesis and processing, transport mechanisms and current state of the art membrane performance. Most importantly, the recent development and novel concepts for improving the hydro-stability and separating performance of silica membranes for desalination are critically examined. Research into silica based membranes for desalination has focussed on three primary methods for improving the hydro-stability. These include incorporating carbon templates into the microporous silica both as surfactants and hybrid organic-inorganic structures and incorporation of metal oxide nanoparticles into the silica matrix. The literature examined identified that only metal oxide silica membranes have demonstrated high salt rejections under a variety of feed concentrations, reasonable fluxes and unaltered performance over long-term operation. As this is an embryonic field of research several target areas for researchers were discussed including further improvement of the membrane materials, but also regarding the necessity of integrating waste or solar heat sources into the final process design to ensure cost competitiveness with conventional reverse osmosis processes.

**Keywords:** desalination; pervaporation; microporous silica; metal oxide silica; hybrid silica; carbon template silica

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## 1. Introduction

Water is essential for life and the rapid increase in the global population, and corresponding urbanization has seen the demand for both the quantity and quality of fresh water increase dramatically. One of the major challenges of the 21st century, if not the most important of all, is water scarcity, with the security of social and economic development of a country closely linked to its water resources. Nearly every industrial sector is dependent upon the availability of water, and water shortages have a resounding impact on all levels of society from the general public to health and politics. Indeed, the major problems encountered by water shortages include drought and famine, loss of production in primary industries, loss of job opportunities, poor health and hygiene as well as an increase in the cost of fresh water. This situation is made more complex by the fact that, according to the World Health Organization, more than 15% of the world's population have no access to potable water and more than 37% have no access to sanitation [1]. Against this backdrop, desalination is becoming an increasingly important tool in the fight to the global demand for clean water.

Membrane technologies have long been an attractive approach to separation in industry, because they are fast and relatively energy efficient processes. In addition, they frequently offer high operational stability, low operating costs and are simple to integrate and control within larger industrial process trains. Indeed, they have been successfully applied to the desalination industry with such vigor that they have long overtaken traditional thermal processes to become the gold standard [2]. In general, there are three main types of membrane processes that are currently applied including reverse osmosis (RO), membrane distillation (MD) and pervaporation (PV) [3]. RO depends on the ability of the 'dense' membrane to repel salt ions whilst allowing the passage of water molecules. The transport is governed by a solution-diffusion mechanism with the driving force being an external pressure difference large enough to overcome the osmotic pressure of the salt water. On the other hand, MD is a thermal process that requires a porous, hydrophobic membrane wherein the passage of water vapour only is permissible. PV, by contrast, uses molecular sieve type of membranes that allows only passage to water molecules but relies on a water vapour pressure difference. Both of these desalination processes require very different types of membranes with vastly different properties and configurations. Currently, there are two main types of membranes for water desalination, namely polymeric (e.g., polyamide-, polysulfone-, polyfurane- and cellulose-based for RO and polytetrafluoroethylene for MD) and inorganic composite or ceramic membranes (alumina-, zirconia-, titania-, zeolite-, silica- and carbon-based). Between these two classes of membranes, polymeric membranes are the most mature and well-established in the desalination industry due to their low cost, manufacturability, simple module design and improved permeability and selectivity [4,5]. However, these membranes suffer from swelling phenomenon, a short life-span due to biofouling as well as poor thermal and chemical resistance [2].

Inorganic membranes, on the other hand, are more resistant to process conditions. In addition, they are by their very nature, porous and hence desalinate via different transport mechanisms to polymeric membranes, based primarily on their pore size. In particular, zeolites and amorphous silica based membranes are attractive candidates for water desalination due to the advantages of their tunable pore sizes and morphology thereby offering higher selectivity. Furthermore, interest in amorphous silica based membranes is gaining momentum because of their simple fabrication techniques, relatively low cost and excellent molecular sieving properties as demonstrated in studies where they are utilized to

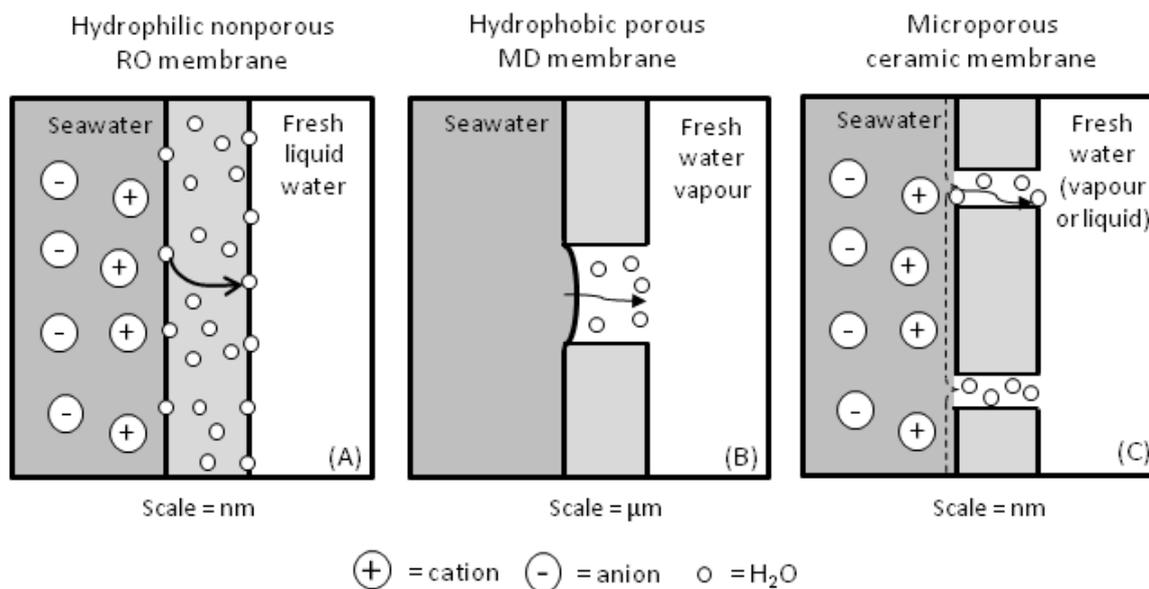
separate gas molecules [6–9]. In these cases, microporous silica membranes have molecular-sieving structures with pore sizes on the order of the kinetic diameter of the species to be separated ( $d_p = 3\text{--}5 \text{ \AA}$ ) and therefore the membrane acts via PV as selective barrier between the water molecule ( $d_k = 2.6 \text{ \AA}$ ) and the hydrated salt ions (e.g.,  $\text{Na}^+$ :  $d_k = 7.2 \text{ \AA}$  and  $\text{Cl}^-$ :  $d_k = 6.6 \text{ \AA}$ ) [10,11], thus allowing the separation of water and salt. However, due to the amorphous nature of the silica material, when exposed to water the silica matrix may undergo dissolution and/or densification [12]. This is a major problem for using silica based membranes in desalination as the effect decreases the overall separation performance and ultimately the quality of the desalinated water. Therefore, a concerted effort has been devoted to improving the hydro-stability of these membranes for various industrial applications.

Many recent reviews have been published for membrane desalination and desalination technologies which are both exhaustive and comprehensive [2,4,5,13–16]. Amongst them, polymeric membranes and zeolites have played a major role. Thus, the contribution of this review is to cover recent studies of non-crystalline microporous silica based membranes for desalination and the new strategies focusing on improving hydro-stability and membrane properties for potential water desalination applications.

## 2. Membrane Processing and Transport Mechanisms for Water Desalination

Water desalination is a process in which fresh water is extracted from aqueous solutions such as seawater, brackish water and brine, which contain dissolved salts and other minerals. For water molecules to diffuse through a membrane, a driving force must be established, otherwise water molecules will remain mixed in the aqueous salt solution. The driving force is associated with concentration, pressure and temperature difference between the feed and permeate sides of the membrane. In the case of RO processes, the water molecules must overcome the osmotic pressure to diffuse through dense polymeric membranes. As the osmotic pressure of typical saline solutions ranges from 0.2 MPa to 3 MPa for brackish water to seawater respectively, RO desalination processes are generally pressure intensive with pressures of between 6 MPa and 8 MPa commonly used for seawater applications [4]. In contrast, MD does not attempt to overcome the osmotic pressure and so does not require a pressurised feed, although being a thermal process the water flux is proportional to the vapour pressure difference across the membrane. MD generally uses porous hydrophobic membranes, where pore size ranges between  $1 \mu\text{m}$  and  $100 \text{ \AA}$ , and the water vapour permeating via the pores is subsequently condensed downstream to produce fresh water [17]. MD operates at lower temperatures (up to  $70 \text{ }^\circ\text{C}$ ) when compared to conventional thermal process such as multi-stage flash or multi-effect distillation. Finally, the PV process, when applied to desalination, employs molecular-sieving ( $d_p = 3\text{--}5 \text{ \AA}$ ) ceramic membranes with a narrow pore distribution smaller than the diameter of the hydrated salt ions ( $>6 \text{ \AA}$ ). Therefore they have the potential to completely reject salt ions while permitting water molecules to permeate. MD and PV are similar processes that can be chiefly identified by the way in which the membrane functions. If the membrane is simply a support structure that allows a meniscus to form on the feed side and plays no role in separation then the process is MD. If however, the membrane actively participates in the separation process then the process is PV. To further provide clarity between these three membrane processes, Figure 1 shows a diagram as comparison of RO, MD and PV in desalination processes.

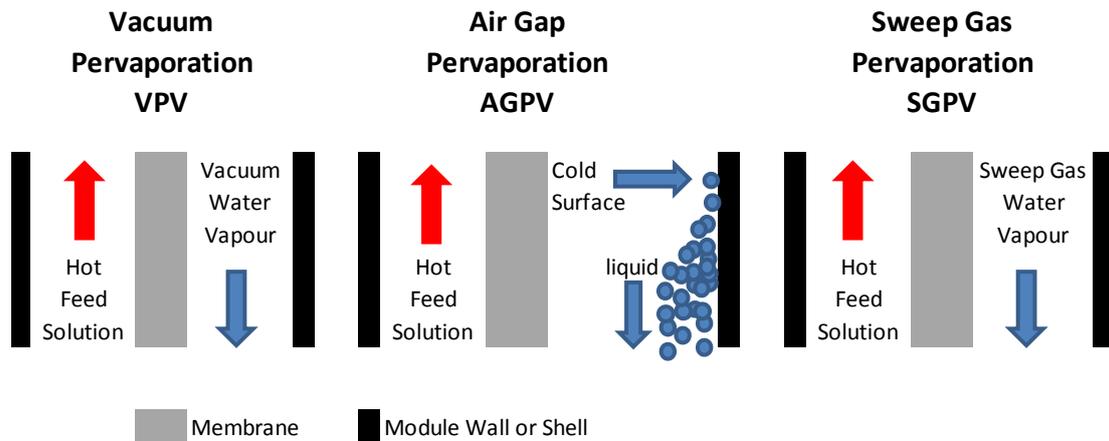
**Figure 1.** Schematic representation of transport mechanism through a membrane via (A) reverse osmosis, (B) membrane distillation and (C) pervaporation for seawater desalination [3].



PV is a well-established water separation technique particularly in alcohol dehydration, although under those circumstances dense polymeric membranes are typically employed [18]. In PV separation processes, the transport resistance is governed by the sorption equilibrium and mobility of water molecules in the silica membrane based on a molecular sieving mechanism [3,15,16,19,20]. Therefore, the transport of the larger hydrated salt ions is excluded through the membrane [21]. In a typical PV process, the membrane acts as a molecular scale selective barrier between the two phases which consist of the liquid phase in the feed and the vapour phase in the permeate side. In order to create a driving force, vacuum is applied on the permeate side of the membrane while the feed side is kept at atmospheric pressure and temperature. The water molecules permeate through the membrane to the exclusion of the salt ions, evaporate on the permeate side and are then convectively transported to the condenser. Fundamentally, the condenser functions to reduce the water vapour pressure on the permeate side by changing the water phase from vapour to liquid. This function allows for a steady state driving force to be maintained throughout the PV operation.

Similar to MD, PV can operate in several different arrangements. The most common MD operational arrangements have been well reviewed elsewhere [17]. The most common PV arrangements are shown in Figure 2 to provide context and include: (i) vacuum; (ii) air gap and (iii) sweep flow. PV can operate using any setup that allows a vapour pressure gradient to form but does not allow the permeate to flow back into the feed.

**Figure 2.** Pervaporation (PV) processes in various operational arrangements.



The PV process variables that are commonly investigated include temperature, pressure, total dissolved solids concentration and the ionic strength of the feed solution. The effect of these variables on water transport through the membrane is measured by two important factors which determine the overall membrane performance: (1) flux of the water and (2) selectivity or rejection of the salt ions. The permeate water is captured in a condenser and the flux ( $\text{kg m}^{-2} \text{h}^{-1}$ ),  $F$ , of water during a given period of time is calculated using Equation (1):

$$F = \frac{M}{S.t} \tag{1}$$

where  $M$  is the permeate mass (kg),  $S$  is the membrane surface area ( $\text{m}^2$ ) and  $t$  is the testing time (h). The salt rejection (%),  $R$ , of the membrane is determined by using Equation (2):

$$R = \frac{C_f - C_p}{C_f} \times 100\% \tag{2}$$

where  $C_f$  and  $C_p$  are the salt concentrations in the feed and permeate solutions, respectively, measured from solution conductivity. Both of the equations are used prolifically in the literature to provide comparison measure for the overall membrane performance in both MD and PV experiments for water desalination. Based on the theory of MD and PV, the salt rejection should equate to 100% since the salt ions will not vapourise under the typical testing conditions. Instead they will crystallize on the inner surface of the membrane on the permeate side if they also find passage across the membrane. There are several reasons that this could occur, but for silica-based membranes this is primarily the result of imperfections in the top layer as a result of poor membrane preparation or silica disintegration in the aqueous environment. Therefore, several research groups have taken this into account by flushing the permeate salt when determining the overall salt rejection [19,22].

As previously alluded to, amorphous silica membranes present an interesting classification problem for membrane desalination technologies, because despite being porous, the water transport through the membrane cannot be described as a conventional MD. One of the major reasons is that in PV using silica based membranes, the pore sizes are too small to effectively form a meniscus associated with a liquid surface tension as it is the case in MD processes. In this case, the Kelvin equation for the liquid-vapour equilibrium is not applicable, as the pure liquid saturation pressure above a convex

liquid surface is essentially the same as the pressure above a flat surface. In other words, the pressure of the water molecules at the pore entrance is possibly the same as in the feed bulk liquid phase (*i.e.*, hydrostatic pressure). Having said that, silica based membranes for PV desalination cannot truly be described as activated transport either, as is the case for these membranes in gas separation [23]. Increasing feed bulk liquid pressure results in almost no water flux changes [19] as expected because changing the bulk feed pressure has a negligible effect on the vapour pressure of the feed; yet changing the vapour pressure of the feed, by increasing its temperature, delivers water flux improvements. Hence, in this case PV closely complies with Darcy's law ( $N = K \Delta P^\circ$ ) where the water flux ( $N$ ) is proportional to the water vapour pressure ( $\Delta P^\circ$ ) and coefficient  $K$ , which are in turn temperature dependent. Silica derived membranes are hydrophilic materials and the water transport can be described by a sorption-diffusion mechanism. In the case of silica-based membranes for PV, water molecules must preferentially access the pore entrances of the silica matrix to permeate through the membrane, a surface adsorption process. Hence, the water transport can be summarised in four successive steps, namely, (1) selective surface adsorption from the bulk liquid mixture, (2) selective access of water to the pore entrance at the membrane interface on the feed side, (3) diffusion of water from the feed side to the permeate side, (4) desorption of water into vapour phase at the membrane interface of the permeate side. Therefore, the physico-chemical properties of the silica membranes as well as their interaction with the water molecules are equally influential.

### 3. Features of Silica Based Membranes for Desalination

#### 3.1. Features of Silica Based Membranes for Desalination

Amorphous silica materials that can be tailored to pore sizes in the range of 3–5 Å are highly suitable for selective membranes in water desalination applications. Several techniques have been widely developed to effectively control the pore size of silica derived membranes, including sol-gel methods [24–31] and chemical vapour deposition (CVD) [32–35]. Although remarkable progress in gas separation applications have been reported using both methods, to date only silica membranes derived via sol-gel processes have been investigated for desalination applications. One of the major reasons is that the sol-gel method is one of the most simple and cost effective routes, which still offers the flexibility to tailor the required porosity. Traditionally, the sol-gel method is a wet chemical process to fabricate metal oxide powders starting from a chemical solution which acts as a precursor for an integrated network (gel). This method is frequently adopted in membrane synthesis or membrane pore modification due to its controllability and homogeneity [24,30,36–38], and it includes various steps such as sol preparation, gel formation, drying and thermal treatment. Many types of silicon alkoxide precursors have been utilized, but the clear majority of research describes work using tetraethoxysilane (TEOS) [39–41]. The sol gel synthesis has been well described in a variety of reference materials [42], and so briefly it involves the hydrolysis (Equation (3)) and condensation reactions (Equations (4) and (5)) of a metal alkoxides to form a network. In the hydrolysis reaction, the alkoxide groups (OR, where R is an alkyl group,  $C_xH_{2x+1}$ ) are replaced with hydroxyl groups (OH). The silanol groups (Si-OH) are subsequently involved in the condensation reaction producing siloxane bonds (Si-O-Si), alcohols (R-OH) and water. The desired microporous structure of the silica layer is thus partially

determined by both the reactivity and the size of the precursors, but also by the appropriate selection of the precursor, water, alcohol and catalyst concentrations.



Hydrolysis and condensation reactions are commonly catalysed by the use of a mineral base or acid. In the case of a silicon alkoxide, acidic conditions usually produce sols with fractal-like structures which have been shown to be more favorable for the formation of microporous silica with smaller pore sizes [38]. Indeed, when the fractal dimension of those species is low enough, their interpenetration is not restricted during the gelation stage, which gives rise to the formation of weakly-branched structures with small pores [42]. By contrast, basic conditions will otherwise favour the production of highly branched fractal structures and/or colloidal particles. This leads to the production of networks with larger pore sizes and is generally not used to prepare molecular sieving silica membranes.

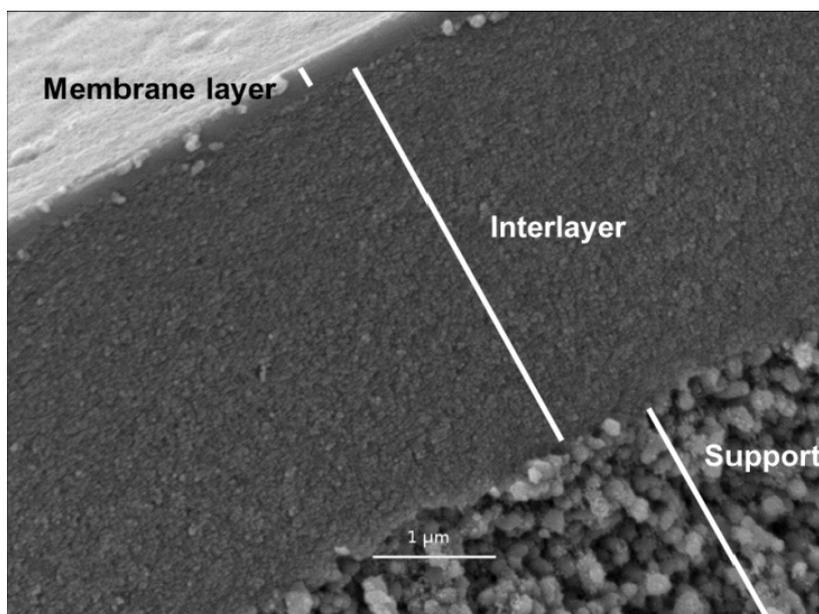
### 3.2. Membrane Preparation

Silica membranes are ultra-thin films (~250 nm) that are traditionally prepared on top of a support for mechanical strength to form an asymmetric structure (as depicted in Figure 3). The support quality plays a major role in the final morphology of the silica derived films as its homogeneity is fundamental in preparing thin films without defects. To achieve this aim, the substrate must have (i) small pore sizes, (ii) low surface roughness and (iii) low defect or void concentration [43]. Substrates with large pores, voids and rough surfaces tend to induce mechanical stress in the films resulting in micro-cracks or pin-hole defects. In order to overcome support roughness, interlayers with smaller pores sizes are typically employed. According to the literature, only a few combinations of support and interlayers have been explored for silica-based membranes for PV desalination. Indeed, supports prepared from  $\alpha\text{-Al}_2\text{O}_3$  powders are currently the substrates of choice due to their high porosity and relatively low cost and high mechanical stability. Mesoporous  $\gamma\text{-Al}_2\text{O}_3$ , consisting of much smaller pore sizes of ~4 nm are as used in 2  $\mu\text{m}$  thick intermediate layers, and are able to minimize the defect rate observed [44]. However,  $\gamma\text{-Al}_2\text{O}_3$  exhibits low hydrothermal stability [45], which is of concern if these materials are to be used in applications containing water vapour. Alternate intermediate layers include silica-zirconia composites developed by Tsuru and co-workers [46,47], which are typically more hydro-stable than  $\gamma\text{-Al}_2\text{O}_3$  layers.

The coating of the substrate (or support) using the sol-gel process can be carried out by dip coating, spin coating and the pendulum method. Due to its flexibility to coat both flat and tubular geometries, in addition to small or large substrates, dip coating has been the preferred process to prepare silica based membranes. Scriven [48] extensively reviewed the dip coating process and proposed five stages: immersion, start-up, deposition, drainage and evaporation. Upon immersion of a substrate to a silica sol, the sol starts adhering to the surface of the substrate. During the withdrawal step, the sol deposits on the surface of the substrate leading to drainage of excess liquid and evaporation of the sol to forming a gel on the support surface. Brinker *et al.* [49] proposed that there is a sequential order of structural development that results from drainage accompanied by solvent evaporation, continued condensation reactions and capillary collapse. According to Brinker *et al.* [50] the concentration of the

deposited film increases 18–36 fold due to evaporation. This causes the formed film to undergo very fast gelation and drying, thus suggesting structural reorganization of the film matrix.

**Figure 3.** SEM micrograph of the cross-section of a high quality asymmetric membrane structure—Reproduced by permission of The Royal Society of Chemistry (<http://dx.doi.org/10.1039/B924327E>) [51].



The withdrawal speed of the substrate from a sol, in addition to the viscosity of the sol, plays an important role in determining the silica thin film formation. Generally, withdrawal speeds reported by several research groups vary between 1 and 20  $\text{cm min}^{-1}$ , whilst prepared sols are diluted with ethanol up to 20 times the original sol volume. In this case (low withdrawal speed and low viscosity), the thickness of a film ( $h$ ) is proportional to  $U^{2/3}$  (where  $U$  is the product of the viscosity and withdrawal speed), in accordance to the Landau and Levich equation [52]. Hence, increasing the speed of withdrawal in the dip coating process will yield thicker films and vice versa. As the production of thicker films tends to lead to cracking upon evaporation and gelation, thinner sols of low viscosity with low withdrawal speeds are preferred.

Upon film coating, the membranes are calcined at high temperatures, generally up to 600 °C, in order to fix the silica structure. Higher temperatures tend to densify the silica film, resulting in extremely low fluxes. The calcination process can lead to thermal stresses between the substrate and the thin silica film, possibly causing film cracking and defects. Hence the heating ramp rate is of considerable importance and is typically low at around 1  $^{\circ}\text{C min}^{-1}$ , although recent developments in rapid thermal processing for silica membranes in other applications are challenging this long held view [53,54]. As the thickness of the silica films are generally in the region of 30–50 nm, and possibly a single film may contain defects caused by either inhomogeneity in the support or interlayers, or calcination stresses, or environmental dust; the dip coating and calcination process is generally repeated at least 2–3 times to produce high quality membranes. As environmental dust affects thin film formation, de Vos and Verweij [55] demonstrated that the quality of silica membranes was greatly improved by simply coating in a clean room environment.

## 4. Novel Silica Based Membranes in Desalination

### 4.1. Hydro-stability and Current Strategies

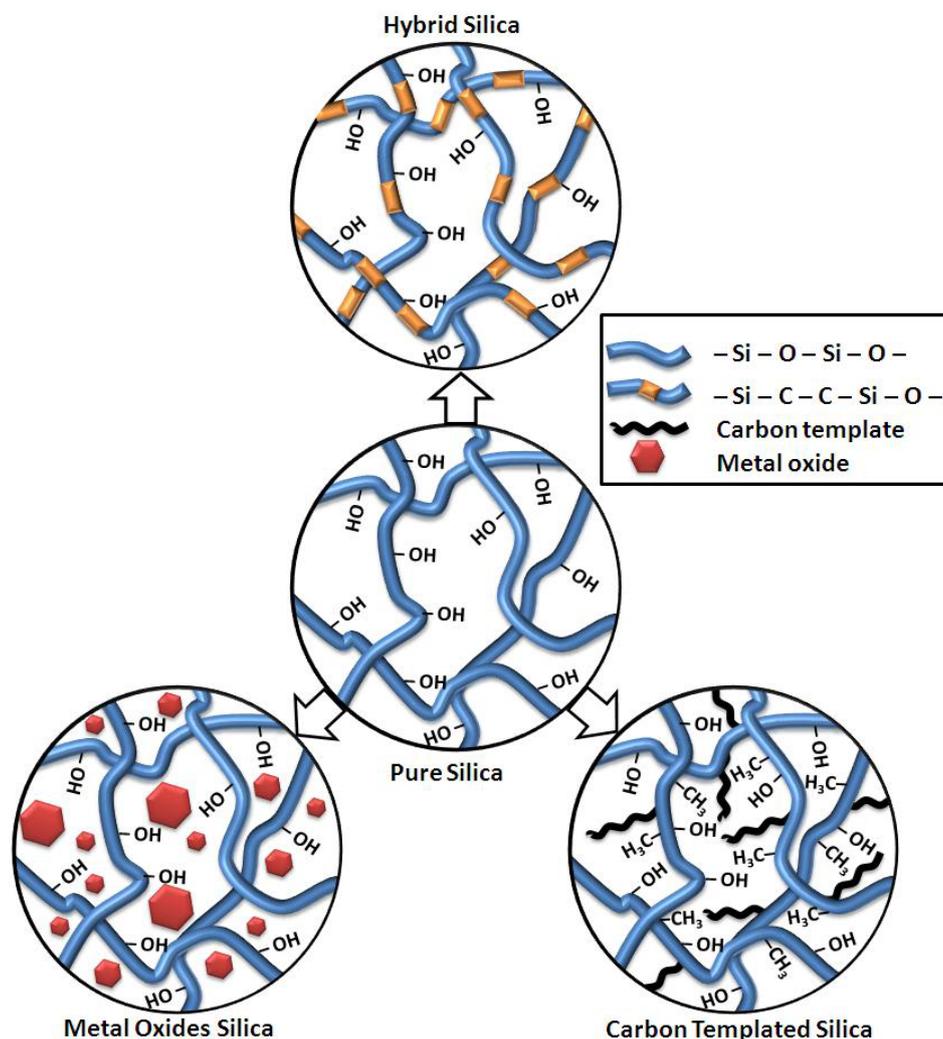
Owing to the affinity of amorphous silica for water adsorption, silica derived membranes undergo structural degradation when exposed to water, leading to a loss of selectivity [56]. Briefly, silica surface materials are prone to rehydration via a mechanism of physisorption of H<sub>2</sub>O molecules on silanol groups (Si-OH), followed by reaction with a nearby siloxane (chemisorption) [57,58]. As a result, H<sub>2</sub>O assists the breakage of siloxane groups, allowing for dissociative chemisorption via the hydrolysis reaction (the reverse of Equation (5)) [59]. Therefore, hydrolysed surface siloxanes may become strained, which act as strong acid–base sites, having a rapid uptake of water and becoming mobile [60]. As the silica seeks to reduce its surface energy under hydrothermal conditions [61], Duke and co-workers [60] proposed that the mobile and strained hydrolysed siloxane groups migrate to smaller pores where they undergo re-condensation to block the pore, whilst the larger pores become even larger. Hydro-stability is therefore a serious problem for the deployment of silica based membranes for water desalination. To address this problem, researchers have attempted to modify the surface properties of the silica, to minimize the interaction of water molecules with the membrane structure. A summary of the main strategies employed is displayed in Figure 4.

One strategy to solve this challenging problem is introducing non-covalently bonded, organic templates into the pure silica matrix [62–64]. Indeed, the presence of carbon moieties embedded into the silica framework can prevent the mobility of soluble silica groups under hydrolytic attack and consequently inhibits micropore collapse. This was demonstrated by Duke *et al.* [60] who successfully prepared carbonized-template molecular sieve silica membranes (CTMSS) by introducing the ionic surfactant (C6 hexyltriethyl ammonium bromide) during the silica sol synthesis. The carbon moieties trapped in the CTMSS matrix were formed by carbonization of the surfactant under vacuum or an inert atmosphere, leading to a hybrid silica/carbon membrane. Although CTMSS membranes still retained their hydrophilic properties, the resultant membranes showed great potential for attaining hydro-stability without compromising the selectivity for wet gas separation [65]. Based on this approach, CTMSS membranes were subsequently tested for desalination performance, demonstrating high salt rejection from seawater [19].

In a similar study, Wijaya *et al.* [66] investigated the effect of the carbon chain length of ionic surfactants in CTMSS membranes for desalination by preparing sol-gels with hexyltriethyl ammonium bromide (C6), dodecyltrimethyl ammonium bromide (C12) and hexadecyltrimethyl ammonium bromide (C16). It was found that the CTMSS membrane prepared with the surfactant with the longest carbon chain (C16) delivered the highest salt rejection, whilst also given the largest pore volume and surface area, although interestingly, the average pore sizes were similar for the three surfactants used. These results suggest that the embedded carbon has a beneficial role in silica matrices and the amount embedded has a direct impact in terms of desalination performance, since the carbon content of the added surfactant is directly related to the amount of carbon remaining following carbonization. However, if the concentration of ionic surfactants is too high they form micelles [67] which drastically limits the possibility of using the sol-gel to dip coat substrates. In order to increase the carbon content in the silica framework, Ladewig *et al.* [68] proposed the use of a non-ionic surfactant such as a tri-block

copolymer like polyethylene glycol–polypropylene glycol–polyethylene glycol (PEG-PPG-PEG), a high molecular weight polymer. Silica samples were mixed with 1–20 wt % PEG-PPG-PEG, and increasing the loading of the tri-block copolymer to 10 wt % effectively doubled the pore volume and surface area compared to pure silica, whilst still maintaining microporosity. Further increases in tri-block copolymer loading to 20 wt % altered the structure of the CTMSS materials to produce mesopores. Of greatest relevance to both the preceding studies and future research directions, the CTMSS membranes prepared with 10 wt % PEG-PPG-PEG (*i.e.*, the highest carbon content sample, whilst still remaining microporous) also delivered high salt rejections and water fluxes.

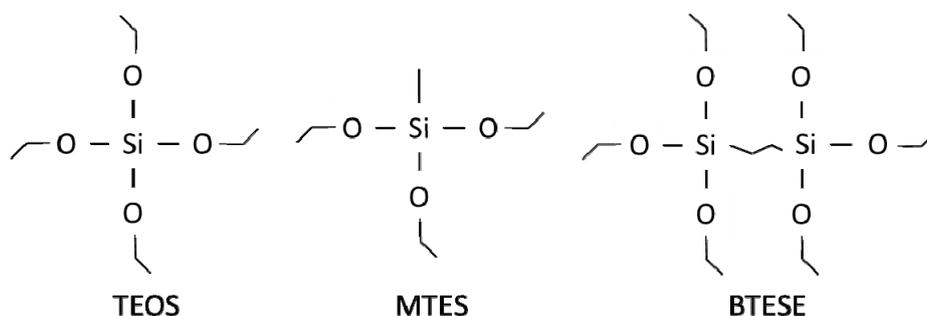
**Figure 4.** Schematic representation of various strategies for silica modification.



Another approach to increase the hydrothermal stability of the pure silica membrane is by incorporating terminal methyl groups ( $\equiv\text{Si}-\text{CH}_3$ ) via various precursors used during the sol-gel synthesis (Figure 5). This was firstly reported by de Vos *et al.* [69] who synthesized methylated silica membranes derived by the copolymerization of TEOS and methyltriethoxysilane (MTES) in the presence of ethanol and water, with an acid catalysis. Again, the membranes were calcined under a non-oxidising environment to retain the carbon moieties in the silica matrix. These membranes showed remarkable stability for alcohol dehydration for 18 months, though severe degradation occurred at testing temperatures of  $\geq 95$  °C thereafter [70]. Although the addition of methyl ligand groups to silica

rendered hydrophobicity, the counter effect was the formation of larger micropores. Duke *et al.* [19] investigated the effect of both methyl ligand and non-ligand C6 surfactant as templates in silica membranes for desalination. They found that the CTMSS membrane outperformed the methylated-silica membrane, suggesting that carbonizing the C6 surfactants led to the formation of smaller pores than the covalently attached methyl groups.

**Figure 5.** Precursors used for the preparation of pure (TEOS), methylated (MTES) and hybrids (BTESE) silica membranes.



Following on from the methyl ligand work, significant hydrothermal improvement can be achieved when the siloxane bridges (Si-O-Si) are partially replaced by organic bridges (Si-CH<sub>2</sub>-CH<sub>2</sub>-Si) such as BTESE in Figure 5. In this method, alkyl groups (ethylene groups in Figure 5) between Si atoms, which cannot be hydrolyzed, can be used as a “spacer” to control the silica network size while minimizing the hydrophilicity of the silica pore surface. The sol synthesis for such membrane layers was first developed by Castricum *et al.* [71] and consisted of a two-step acid hydrolysis of BTESE/MTES mixtures. In this work they showed that the durability of the membrane network for the dehydration of n-butanol by PV was greatly improved by incorporating hydrolytically stable organic groups as integral bridging components into the nanoporous silica. These hybrid organosilica membranes were able to withstand long-term PV operation of up to 2 years at 150 °C. Recently, Tsuru *et al.* reported the potential of such BTESE membranes in RO and PV desalination processes [72].

Alternate efforts have focused on modifying the silica structure through the addition of metal oxides [73–77]. Recently Lin *et al.* [21] reported for the first time the potential of cobalt oxide silica (CoOxSi) membranes for desalination of waters from brackish to brine concentrations. CoOxSi xerogels were synthesised via the sol-gel method using TEOS, cobalt nitrate hexahydrate and hydrogen peroxide, at a range of pH from 3 to 6. The pH was altered by addition of ammonia during the sol-gel process. Initial hydrothermal exposure (<2 days) at 75 °C of xerogels resulted in the reduction of pore volume and surface area, although subsequent exposure proved that the pore structure of the xerogels was no longer significantly altered. The CoOxSi synthesized at pH 5 was the most resistant to the hydrothermal degradation, remaining stable and delivering high salt rejections for 570 hours of testing at temperatures up to 75 °C and NaCl salt concentrations up to 15 wt %.

#### 4.2. Membrane Performance: Effect of Testing Conditions

A summary of the reported membranes performance in term of water flux and salt rejection is listed in Table 1. It must be stressed that comparing these results gives an indication of the general

performance only. One should be aware of that these results are dependent upon several parameters related to testing condition including feed concentration, salt used, feed temperature, feed flow rate, cross-flow velocity, permeate vapour pressure and fouling/scaling tendencies. In addition, these listed membranes may have different geometries (flat or tubular and sizes) and architecture (thickness of top film, number interlayers number, porosity and substrate). As such, all these factors play a role in the final performance of the tested membranes.

**Table 1.** Performance comparison of silica based membranes for desalination.

Membrane type	Testing conditions (Temp., Pressure)	Feed conc. range (wt %) Lower/Higher	Water flux (kg m <sup>-2</sup> h <sup>-1</sup> )	Rejection (%)	Stability Tests	Reference
Carbonized template CTMSS	Ionic C6	20 °C, P = 7 bar <sup>a</sup>	0.3/3.5*	2.1/1.9	99.9/98	5h [19]
	Ionic C6	20 °C, ΔP < 1 bar <sup>b</sup>	0.3/3.5	3.2/1.4	86/92	N/A [66]
	Ionic C12	20 °C, ΔP < 1 bar <sup>b</sup>	0.3/3.5	2.8/1.6	84/94	N/A [66]
	Ionic C16	20 °C, ΔP < 1 bar <sup>b</sup>	0.3/3.5	3/2	91/97	N/A [66]
	10 wt %	20 °C, ΔP < 1 bar <sup>b</sup>	0.3/3.5	1.5/1.5	90/99.8	12 h [68]
	PEG-PPG					
	20 wt %					
PEG-PPG	20 °C, ΔP < 1 bar <sup>b</sup>	0.3/3.5	6.3/4.9	87/97	12 h [68]	
Metal oxide	CoOxSi	20 °C, ΔP < 1bar	0.3/15	0.4–0.3	99.7/99.9	570 h [21]
		50 °C, ΔP < 1bar	0.3/15	0.9/0.35	99.5/99.9	570 h [21]
		75 °C, ΔP < 1bar	0.3/15	1.8/0.55	99.5/99.9	570 h [21]
Hybrid	BTESE	30 °C, ΔP < 1bar	0.2	3	99	N/A [7]
	BTESE	90 °C, ΔP < 1bar	0.2	34	99.9	N/A [7]
	MTES	20 °C, P = 7 bar <sup>a</sup>	0.3/3.5*	4.7/2.5	93.7/83	5 h [19]

<sup>a</sup> Feed pressurizing up to 7 bar and permeate vacuum pumping; <sup>b</sup> Permeate vacuum pumping, resulting in a pressure difference ΔP across the membrane less than 1bar; \* Sea water.

The majority of membranes listed in Table 1 were tested for feed synthetic solutions containing NaCl dissolved in deionised water with concentrations ranging from 0.3 to 3.5 wt % in order to simulate the typical salt concentration of brackish water (0.3–1 wt %) and sea water (3.5 wt %). CTMSS membranes gave similar water fluxes varying from 1.4 to 6.3 kg m<sup>-2</sup> h<sup>-1</sup> with high salt rejections greater than 84%, depending on the operating conditions. Hybrid membranes (*i.e.*, those prepared with terminal methyl groups or covalently bound carbon bridges) also gave similar water fluxes and salt rejections. The hybrid membranes prepared with BTESE delivered considerable high water fluxes at 34 kg m<sup>-2</sup> h<sup>-1</sup> at 90 °C and excellent salt rejection 99.9%. However, these membranes were tested at very low salt concentration (NaCl 0.2 wt %) and high feed temperature and when cooler feed temperatures (30 °C) were used, the water fluxes reduced considerably (one order of magnitude). In the only study of its kind so far, CoOxSi based silica membranes were also investigated for brine processing conditions where the salt concentrations ranged from 7.5 to 15 wt %. In this case, an increase in salt concentration in the feed from 0.3 to 15 wt % resulted in a decline of the permeate flux from 1.8 to 0.55 kg m<sup>-2</sup> h<sup>-1</sup> at 75 °C. However, despite the high salt feed concentrations, the salt rejection remained high suggesting they were stable under these harsh testing conditions.

Analysing the results reported in Table 1, the trends are very clear with increasing temperature yielding increased water flux whilst increasing salt concentration results in decreasing water flux. For instance,

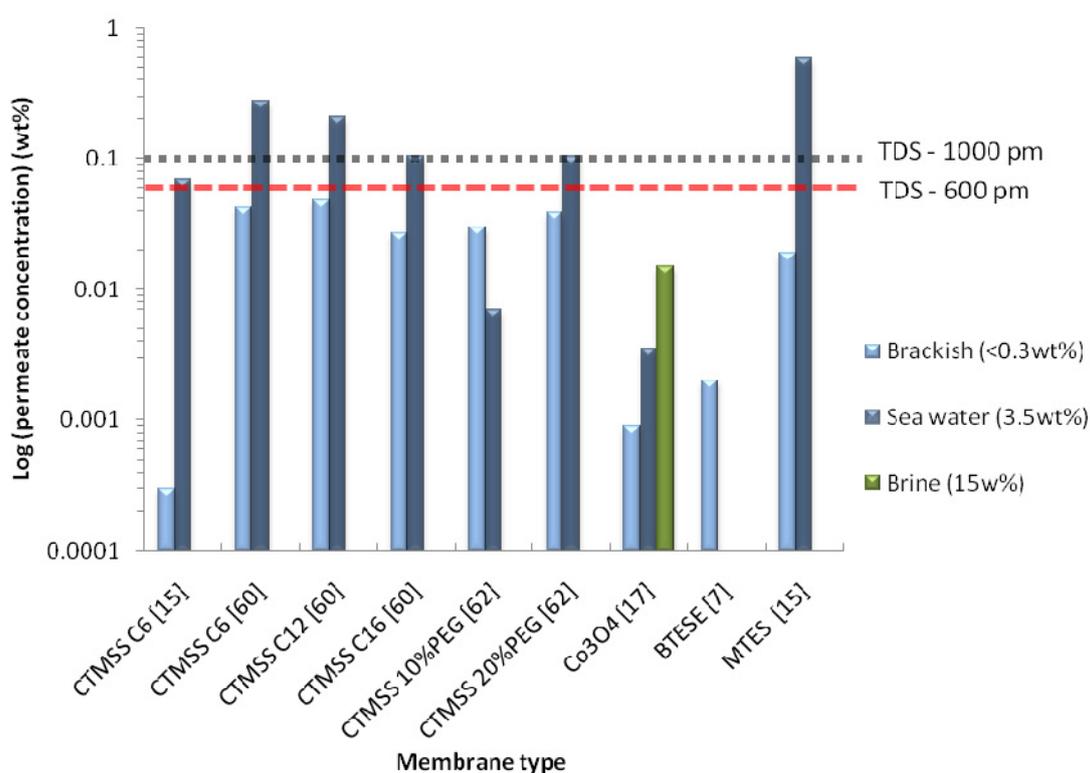
at 0.3 wt % salt feed concentration, the water flux increased by 77% (from 0.4 to 1.8 kg m<sup>-2</sup> h<sup>-1</sup>) as the feed temperature was raised from 20 °C to 75 °C. This can be explained through the thermodynamics of the system in that as the temperature increases, so does the water vapour pressure in the feed stream, leading to an increase in the driving force for water permeation across the membrane. Likewise the water vapour pressure decreases as a function of the salt concentration, partially explaining the decreased flux observed under seawater and brine feed concentrations. However, the water vapour pressure change as a function of the salt concentration at constant temperature is not large enough to justify the large reduction of flux as reported by several groups in Table 1. For instance, in the case of carbonized template CTMSS (ionic C6), experiment was conducted at a fixed temperature of 20 °C [68]. Indeed, water flux was reduced by more than half (56%) by increasing the feed concentration from 0.3 wt % to 3.5 wt %. In that case, the change in vapour pressure driving force of an ideal salt solution will change from 2.3 kPa to 2.28 kPa, representing a decrease of 0.08% [78] far smaller than the decline in flux, thus demonstrating that salt and temperature polarization are also likely occurring. In this case a boundary layer of more concentrated salt forms at the membrane surface due to the permeation of water through the membrane being faster than the diffusion for fresh water from the bulk to the membrane surface. Likewise thermal boundary layers can form through the conduction and convection of sensible heat and the transfer of latent heat through the vapourisation of water through the membrane. This phenomenon, along with temperature polarization, is commonly observed for MD processes. Interestingly, temperature polarization, whereby the heat flow across the membrane from conduction and convection is sufficient to reduce the temperature at the membrane surface in comparison to the bulk feed, is the more commonly reported problem [79]. The fact that salt concentration polarization is strongest suggest that (a) the silica-based membrane is more insulating than typical polymeric MD counterparts, and that (b) the cross flow velocities investigated were not sufficient to disturb or reduce the mass transfer boundary layer.

The purity of the water in the permeate stream is a fundamental parameter in terms of potable water. As the salt rejection is generally a ratio of salinities (Equation (2)), a high salt rejection for a high feed salt stream does not necessarily translate into potable water. According to the World Health Organization potable water should have a factor called total dissolved solids (TDS) < 600 ppm with an upper limit of TDS < 1000 ppm [1]. To assess the performance of the membranes in Table 1 in terms of water quality, the permeate water concentration was calculated as shown in Figure 6. All the membranes listed in Table 1 produce good quality drinking water (TDS < 600 ppm) for slightly saline water conditions (0.3 wt %). However, only the CoOxSi silica base membranes were able to meet the requirement of 600 ppm for seawater and brine feed conditions. For those membranes with TDS in excess of 600 or 1000, a second pass becomes necessary to achieve potable water requirements. As discussed previously the theory of PV operation necessitates that the permeate stream should be free of salt, regardless of the feed conditions.

The observation that the vast majority of silica-based membranes tested under PV desalination conditions do not give pure water in the permeate stream is strong evidence that research focusing on improving the hydro-stability of the silica as well as the integrity of the membrane layer itself should continue to receive high priority. However, only a handful of authors have reported preliminary stability measurements as listed in Table 1. In the longest performance evaluation reported so far, Lin *et al.* sequentially tested cobalt oxide silica (CoOxSi) membranes with solutions containing

salt at 1 wt % (288 h), 3.5 wt % (144 h), 7.5wt % (72 h) and 15 wt % (72 h), leading to a total of 575 hours [21]. Despite a significant variation in water flux observed during the first 120 h, the water flux tended to stabilize after 5 days of measurement. This was attributed to initial textural and/or structural changes in the CoOxSi matrix and was also observed in nitrogen sorption and FTIR analyses. However, this long term testing successfully demonstrated the improved hydro-stability of CoOxSi membranes at several temperature points and feed concentrations. In the only other studies reported thus far, Duke *et al.* reported stable performance over 5 h of the CTMSS (Ionic 6) membrane [19]; and Ladewig *et al.* showed stable performance over 12 h, suggesting the benefit of the carbonized templating method to improve the hydro-stability of amorphous silica membranes [68].

**Figure 6.** Comparison of water quality in the permeate stream.



#### 4.3. Future Challenges

Silica based membranes for desalination applications are still at the embryonic stages of research and development. Therefore, this type of membrane requires significant improvements to be able to compete against both alternate membranes and alternate technologies. Indeed, the RO process using polymeric membranes is now a mature technology, having undergone major research, development and deployment in the last 30 years. This developmental advantage implies that RO will continue to dominate the large desalination plants around the world. However, RO cannot process all feed concentrations, in particular the pressure requirements for brine processing are prohibitive and can even destroy the polymeric membranes. Thus silica based membranes (especially metal oxide silica membranes, such as CoOxSi) operating under PV conditions, could have a niche market in the processing of brines or even the processing or drying of mineral salts such as potash or lithium brines.

In order to be able to compete against polymeric RO membranes, the water fluxes of silica based membranes for processing seawater (NaCl 3.5 wt %) must be significantly increased, by an order of magnitude on average. At the moment high water fluxes in excess of  $20 \text{ kg m}^{-2} \text{ h}^{-1}$  have been demonstrated for BTESE silica membranes only, although only for slightly saline feed concentrations (NaCl 0.2 wt %) and high temperatures at  $90 \text{ }^\circ\text{C}$ . This raises the second major impediment to silica based membrane PV, the issue of temperature, and ultimately energy consumption. PV is a thermal process and raising the temperature of feed translates into higher vapour pressures which should likewise increase water flux and water production. The problem here is that heat must be generated to increase the temperature of the water (and ultimately vapourise it), which together with the energy required to condense the water vapour explains why the PV process uses more energy per liter of water produced than RO processes which use only pump energy to pressurize the saline water feed. If this heat is supplied through conventional means, the cost will be prohibitive. However, there are several options available to reduce the cost of energy by utilising waste heat from industrial sites and thermal power plants, salt gradient solar ponds or solar heat [80–84]. These options may be attractive to deploy PV using silica based membranes.

A vital aspect of any membrane technology is long term operation and stability. At the moment, CoOxSi silica membranes have demonstrated stability up to 575 hours of operation. Similar tests must also be undertaken for CTMSS and hybrid silica based membranes to show proof of concept. To some extent, the CoOxSi silica membranes showed superior performance than MFI zeolites, which may be viewed as a competing membrane technology. In a recent study, Dobrek and co-workers [22] reported the dissolution of both S-1 and ZSM-5 top layers in MFI zeolite membranes after 560 hours testing in PV desalination. This was attributed to the combined effects of ion exchange and water dissolution mechanisms. The loss of membrane performance due to the quality of the saline waters can therefore cause deterioration of the materials such as in zeolite membranes, or fouling and scaling as is the case of polymeric membranes [85]. Currently, there is no fouling work reported for silica based membranes mainly due to the embryonic nature of the testing which has occurred under laboratory conditions using synthetic salt solutions. Given the scale of the problem for RO membranes, this is a problem that will require substantial research to ensure that silica based membranes can be deployed in an industrial context to process saline waters to potable quality.

## 5. Conclusions

Microporous silica based membranes have been shown to provide excellent molecular sieving properties for gas separation applications but their reported use in water treatment processes, such as desalination, have been limited, primarily due to the lack of stability when exposed to water. However, innovative concepts have been developed in the last two decades to realize the potential of silica based membranes for desalination via PV. In particular, research into silica based membrane desalination has focussed on three distinct methods of stabilising the structure including carbon templated silica, hybrid organic-inorganic silica and metal oxide silica. Whilst these methods have all been successfully trialed for desalination via PV, only metal oxide silica membranes have demonstrated significant potential with high salt rejections under all feed concentrations, reasonable fluxes and unaltered performance for over 575 hours of operation. Indeed they were the only membranes capable of producing potable water

from highly concentrated brine feed streams. The target areas of research for membrane scientists is therefore on the materials development to further improve water fluxes (in order to compete with RO processes), to stabilize the silica structure to ensure no reductions in long term performance and to produce defect-free membranes to ensure high salt rejections, at low cost. The final challenge for the membrane research community is to establish the conditions under which PV desalination using silica based membranes is most technically and economically viable. The energy requirements of PV systems are considerable in comparison to RO processes and analysis of the thermodynamics indicates that parity will never be reached when utilizing primary energy sources. However, if PV processes are successfully integrated with waste heat or solar heat sources then the technology may be attractive for niche applications such as brine processing or salt recovery. Regardless, the separation and purification of potable water from desalination is a paramount task which the membrane research community must endeavour to address before water supply becomes a global crisis.

### Acknowledgments

Muthia Elma specially thanks for the scholarship provided by the University of Queensland. The authors acknowledge financial support from the Australian Research Council (DP110101185). Simon Smart also acknowledges funding support from the Australian Research Council (DP110103440).

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