Journal of Membrane Science 494 (2015) 68–77

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Nature gives the best solution for desalination: Aquaporin-based hollow fiber composite membrane with superior performance

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ARTICLE INFO

Article history:
Received 4 April 2015
Received in revised form
17 July 2015
Accepted 18 July 2015
Available online 26 July 2015

Keywords:
Aquaporin z
Biomimetic hollow fiber
Thin film composite membrane
High performance

ABSTRACT

Nature has contributed the best selective material, Aquaporin (AQP), for us. Herein we report on a highly permeable and selective hollow fiber composite membrane based on Aquaporin Z. The AQP-incorporated proteoliposomes were immobilized on the inner surface of a hollow fiber membrane substrate and subsequently coated by a polyamide layer formed by a non-gas assisted interfacial polymerization process. Morphological observation suggested that the introduced proteoliposomes were totally embedded in the polyamide layer with their intact spherical shape preserved. Hollow fiber composite membranes with different AQP covering densities were prepared and evaluated, and an elevated covering density of AQPs was found beneficial in improving the water flux and salt rejection of the resultant membrane. The biomimetic membrane with a high AQP covering density exhibited a 40 L m^{-2} h^{-1} permeate flux at 5 bar, almost 200% as much as the flux of a typical commercial reverse osmosis membrane (BW30). This membrane also exhibited above 97.5% rejection to a 500 ppm NaCl solution, which was superior to the commercial membrane tested under the same conditions. Moreover, a forward osmosis test of the AQP-based hollow fiber membrane also yielded a super high water flux without a notable increase in salt back diffusion. It was therefore concluded that the integration between embedded proteoliposomes and the polyamide layer was effectively defect-free, and the remarkably enhanced water permeation was contributed by the embedded AQPs. Furthermore, it was estimated that the newly developed AQP based hollow fiber membrane could reduce the power consumption significantly if applied in a water reclamation process. The AQP-based biomimetic membrane has been designed and fabricated beyond the proof-of-concept stage and is able to offer a novel means for tailoring the membrane materials to enhance membrane performance.

1. Introduction

Water scarcity is now receiving increasing attention worldwide and is becoming more challenging in view of expanding population, climate change and socio-economic activities. The growing demand for safe fresh water is driving much effort to explore more sources of water supply such as water reuse and seawater desalination. This undoubtedly calls for more efficient water treatment technologies. Of these technologies, membrane-based technology has aroused much interest because of its cost-effectiveness over other water treatment technologies. In comparison to other membranes, reverse osmosis (RO) membranes remove almost all impurities including ions and small organic molecules, and are able to provide direct supply of high-quality water. The advancement of thin-film composite membranes has reduced the cost dramatically and made RO membrane technology a fast growing approach for seawater and brackish water desalination, as well as wastewater reclamation [1]. However, further development is still needed given the fact that the energy usage is still 1.5–2.0 times the theoretical minimum dictated by thermodynamics [1,2].

One strategy to further reduce the energy cost is utilizing a novel membrane material which can provide higher water permeability without sacrificing salt rejection [2,3]. Although some new technologies have been applied to improve the performance of membrane materials [4,5], there is room for improvement. In a

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http://dx.doi.org/10.1016/j.memsci.2015.07.040
0376-7388/

landmark paper in 2007, Kumar et al. [6] suggested that the properties of natural 'water channels', known as Aquaporins (AQPs) [7–9] are extremely attractive for desalination, if they could be incorporated into synthetic membranes. AQPs are a group of water channel proteins in cell walls, and can transport as many as 3 billion water molecules per subunit per second with all other solutes rejected [8]. Based on the promising water permeation and solute transport behavior of amphiphilic triblock-polymer vesicles containing Aquaporin Z (AqpZ), isolated from *Escherichia coli*, Kumar et al. postulated that incorporating AQPs into polymeric membranes could lead to high performance water treatment membranes [6].

The enormous potential to develop desalination membranes based on AQPs has attracted extensive research efforts worldwide in the following years. In the initial stage, the AQP based biomimetic membranes were proposed and prepared by a relatively straightforward approach: the AQP-incorporated liposomes (proteoliposomes) or polymersomes were directly fused (as collapsed or folded vesicles) onto a surface of porous substrate to form a dense 'skin' layer [10–14]. It was anticipated that this dense layer could function as a selective layer and the porous substrate could help withstand the applied pressure, similar to the structure of a thin film composite membrane. At the same time the incorporated AQP could facilitate the transport of water molecules, acting as its role in the kidney to contribute a higher water flux. Although some membranes prepared by this protocol showed interesting results, the activity of the AQP was still vulnerable to the external environment and it was challenging to scale-up to produce a large area of defect-free selective layer in this way. Defect formation in the extremely thin selective layer (4–8 nm) composed of lipid or block copolymer molecules remained a challenge for preparing a biomimetic membrane with good performance. Subsequent research has shown that intact vesicles incorporated with AQP had an excellent mechanical strength and stability [15]. Thus, instead of forming a dense layer by vesicle fusion and collapse, another protocol is now emerging where the vesicles with AQPs are immobilized on a porous substrate and subsequently coated by a layer to cover or connect these vesicles [16–20]. This coating layer can be formed either by crosslinking with chemicals, or by layer-by-layer assembly with polyelectrolytes or by polymerization. These layers, together with the vesicles, could function as a selective layer, which determines the water permeability and salt rejection. In contrast to the earlier protocol, this method has the potential to reduce the formation of defects, which is critical issue for desalination or water reclamation. However the layers constructed by chemical crosslinking, layer-by-layer deposition, or polymerization tend to be rather thin, which still leaves a chance for the defect formation and passage of salt. This is probably the main reason why these reported membranes have been prepared with extremely small areas, and would not be readily scaled-up.

Our group developed a new method to solve this problem where the proteoliposomes are totally embedded into a dense layer formed by a conventional interfacial polymerization [21] or crosslinking method [22]. The dense selective layer encapsulated the immobilized proteoliposomes, and thereby efficiently eliminates the formation of defects. However, although our preliminary results showed that the embedded proteoliposomes did improve the performance of the membrane to some extent, the increment was quite modest compared to the promising high permeability of AQPs. One possible reason responsible for the modest increase in water permeation could be the influence from the in-vitro environment, such as lipid, detergent and additive [15,23,24], that affected the protein-to-lipid ratio (PLR) or the activity of AQPs, resulting in a decline of the proteoliposome permeability. Optimization of proteoliposome system is important and necessary to achieve a high membrane performance. On the other hand, theoretically, the loading amount of proteoliposomes in the selective layer also determines the performance of the resultant membrane. However, in previous study, some harsh conditions such as strong gas sweeping [21] or high-temperature thermal treatment [22] was used for thin film composite membrane preparation. These operations could induce a significant loss of proteoliposome loading, causing a minor enhancement of water flux and poor reproducibility.

To date, almost all reported AQP based membranes still stagnated on the proof-of-concept stage and none of those protocols could provide a membrane which is competitive with current commercial RO or nanofiltration (NF) membranes in terms of separation performance, scalability or stability [25]. In the present study, we proposed several protocols to fabricate a high performance AQP-based membrane beyond the proof-of-concept. The differences from previous study are summarized as follows: (1) prior to being introduced into membrane, the proteoliposome system was optimized for the highest permeability and the optimal proteoliposome was employed for membrane preparation. (2) A hollow fiber membrane was selected as the substrate instead of the flat sheet membrane as a non-gas assisted interfacial polymerization process could be applied on the hollow fiber membrane substrate. This process avoided using a strong gas sweeping process [21] or thermal treatment process [22] for the thin film formation and thereby minimized the loss of proteoliposomes on the substrate. Additionally, hollow fiber configuration offers many advantages over flat sheet configuration and can be scaled up easily. (3) The use of aggressive chemicals in interfacial polymerization such as strong ionic surfactant was avoided to maintain the activity of the AQPs [23].

The whole procedure is schematically illustrated in Fig. 1. The proteoliposome was first deposited on the inner surface of an ultrafiltration (UF) hollow fiber membrane and then encapsulated within a polyamide layer by interfacial polymerization. This structure ensured a protective environment for the incorporated AQPs, which is critical for remaining the activity of AQPs over the long term operation in practical applications. It is envisaged that this membrane preparation technique could lead to the design and development of a new generation AQP-based hollow fiber membrane for RO and forward osmosis (FO) processes.

2. Materials and methods

2.1. Materials

1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC) was purchased from Avanti Polar Lipids (*Alabaster, AL*). Q-sepharose was purchase from GE (*Singapore*). Polyethersulfone (PES, *Solvay*) was used as the membrane material for the hollow fiber substrate fabrication. N-Methyl-2-pyrrolidone (NMP, $>99.5\%$, *Merck Chemicals, Singapore*) was used as a solvent for dope preparation. m-Phenylenediamine (MPD, ≧99%, Sigma-Aldrich) and trimesoyl chloride (TMC, $>99\%$, Sigma-Aldrich) were used as the monomers for the interfacial polymerization. Sodium chloride (NaCl, *Merck Chemicals, Singapore*) was used to prepare the draw solutions and the feed waters in RO and FO tests. BW 30 membrane was supplied by Dow filmtec (USA). All other chemicals or materials were purchased from Sigma-Aldrich (*Singapore*) unless otherwise stated. All chemicals were used without further purification. Milli-Q water (Millipore, integrated ultrapure water system) with a resistivity of 18.2 MΩ cm was used.

2.2. Liposome preparation

A liposome solution was prepared by a film rehydration