Carbon nanotube immobilized membrane with controlled nanotube incorporation via phase inversion polymerization for membrane distillation based desalination

Smruti Ragunath, Sagar Roy, Somenath Mitra*

Department of Chemistry and Environmental Science, New Jersey Institute of Technology, Newark, NJ 07102, USA

ARTICLE INFO

ABSTRACT

In this paper, we present an optimized method for carbon nanotube immobilization on membrane surface for seawater desalination via direct contact membrane distillation (DCMD). Carbon nanotube immobilized membranes (CNIM) are fabricated via phase inversion technique using a controlled approach for carbon nanotube (CNT) incorporation which provides additional pathways for water vapor diffusion. Surface morphology differed for membranes fabricated with varying PVDF concentrations which altered the CNT distribution and its interaction with water vapor. The water vapor flux by CNIM membrane was as high as 51.4 L/m² hr, which was 76% higher than the unmodified support membrane at 60 °C. No significant salt leakage was observed with modified membrane. The overall mass-transfer coefficient for phase inversion membrane was nearly 1.8 times higher than unmodified membrane.

1. Introduction

Rapid climate changes and other factors have increased the demand for fresh water and consequently the need for desalination technologies for pure water generation [1]. Relatively lower energy requirements, cost and smaller foot prints make membrane based techniques like reverse osmosis (RO), forward osmosis (FO) and membrane desalination (MD) attractive desalination approaches [2,3]. MD is a membrane based thermal evaporative process which operates at relatively low temperatures, can provide high salt rejection and handle high salt concentrations [4–9]. MD has the potential to generate pure water using low grade heat such as waste heat from power plants and solar power [10–12]. The major challenge facing MD is cost reduction to make it commercially viable. Consequently, a major consideration in MD is the membrane itself because it determines both flux and selectivity. Hence fabrication of membranes that can provide enhanced performances is of great interest [13].

Conventional MD membranes include those made of polypropylene (PP), polyvinylidene difluoride (PVDF), polytetrafluoroethylene (PTFE) where techniques such as graft and plasma polymerization have been used to modify surface characteristics [14,15]. A variety of more complex membranes with hydrophobic and hydrophilic surface coatings, or hydrophobic layer sandwiched between two hydrophilic layers have been reported [16–18]. Recent developments have reported fabrication of MD membranes with zeolite, clay nanoparticles, modification with porous alumina and nanocarbon like carbon nanotubes and graphene [19–24]. This includes, self-supporting CNT-Bucky paper membrane prepared by interfacial polymerization and vertically aligned CNT membranes for reverse osmosis (RO) process have been reported [25–27].

We have reported the development of carbon nanotube immobilized membrane (CNIM) with different functionalized forms where the CNTs have been incorporated into the membrane with the help of polymer to serve as an immobilizing agent [28–30]. These techniques have been extended to other nano-carbons such as graphene and nano-diamond as well [31]. CNTs incorporated on the membrane surface act as nanosorbent and provide additional pathways for solute transport. These novel membranes have demonstrated superior performances in diverse applications such as solvent extraction, pervaporation [32–34], desalination [29,30], volatile organic extraction from air, micro extraction [34,35], concentration of pharmaceutical waste [36], and dehumidification [37]. While these membranes have shown excellent performance, there is no way to control the surface morphology.

In an effort to develop the next generation of CNIM, it is important to explore other methods of CNT incorporation where the surface morphology and CNT distribution can be controlled. Phase inversion is a well-known membrane fabrication technique for preparing porous membranes where a polymeric layer can be incorporated via solvent

---

evaporation, precipitation from vapor phase, thermal precipitation, immersion precipitation and dry-wet phase inversion [15,38]. A selective layer can also be created using solvent/non-solvent evaporation approach where a polymer is uniformly dispersed in a solvent/non-solvent mixture and casted on a support. Upon evaporation, the solvent creates a continuous polymeric phase while the non-solvent part creates the voids resulting in a porous layer. The objective of this research was to synthesize CNIM using solvent/non-solvent type phase inversion where the surface morphology and consequently membrane performance can be varied.

2. Experiment

2.1. Materials

Hydrophobic polypropylene (PP) membranes with nominal pore size of 0.45 μm were purchased from Sterlitech Corp., (WA, USA). Multiwall carbon nanotubes (MWNT) were purchased from Cheap Tubes Inc., (Brattleboro, VT, USA). Other chemicals which includes polyvinylidene fluoride (PVDF), acetone and methanol were purchased from Sigma Aldrich (PA, USA).

2.2. Membrane fabrication

Surface modification of polypropylene membrane was carried out by creating a porous selective layer on the surface of the support membrane via solvent/non-solvent evaporation type phase inversion approach [38–40]. Here we used a volatile solvent (acetone) with desirable dispersibility for both polymer and CNTs. Methanol was used as the non-solvent to facilitate pore formation as it had comparatively lower vapor pressure and was immiscible with the PVDF-CNT mixture. Uniform dispersion of casting solution was prepared with pre-weighed amount of PVDF and CNT in acetone followed by the addition of methanol. PVDF-CNT mixture was cast on polypropylene substrate using a casting knife. The cast membrane was allowed to dry at 60 °C in a vacuum oven. After initial trial and error, the acetone to methanol volume ratio was optimized to be 80:20 for fabrication of membranes with different polymer loading. Membranes were cast with well dispersed solution containing varying amount of PVDF from 0.001 to 0.03 wt% while the CNT concentration was fixed at 0.01% based on preliminary trial error experiments.

2.3. Membrane characterization

Surface morphology of the membranes was characterized using scanning electron microscope (SEM) (Leo 1530 VP, Carl Zeiss SMT AG Company, Oberkochen, Germany). The membrane samples were cut to 0.5 cm long pieces and carbon coated for SEM imaging. The elemental composition of the membranes was analyzed using energy dispersive X-ray spectroscopy (EDX). The surface topography and roughness of the membranes was determined using atomic force microscopy (Park NX10 AFM, Park Systems, USA) under ambient conditions. Measurements were obtained in non-contact mode (Park SmartScan™) using silicon-nitride cantilever containing silicon probe with resonant frequency of 50 kHz, tip radius 2–5 nm for a scan area of 5 μm and average surface results has been reported. Furthermore, thermal gravimetric analysis (TGA) to study the thermal stability of modified and unmodified membranes using PerkinElmer Pyris 7 TGA system at isothermal heating rate of 10 °C/min in air.

The effective surface porosity over the effective pore length was measured by gas permeation tests previously reported in other similar studies [41]. The total molar flux per unit trans membrane pressure difference across the porous PP membrane can be described as

$$\frac{J_w}{\Delta p} = \frac{2}{3}\left(\frac{8RT}{\pi M}\right)^{0.5}\frac{1}{RT}\frac{r\varepsilon}{L_p} + \frac{\bar{p}}{8\mu RT}\frac{r^2\varepsilon}{L_p} \tag{1}$$

where ε is surface porosity, r is mean pore radius of the membrane, μ is gas viscosity, R is gas constant, $\bar{p}$ is the average feed and permeate pressure, M is molecular weight of gas, L_p is effective pore length and T is temperature (k). The first term of the equation represents the Knudsen flow and the second term the Poiseuille flow. The gas effective surface porosity over pore length was $e\left(\frac{J_w}{\Delta p}\right)$ can be calculated as,

$$\frac{J_w}{\Delta p} = \frac{N_{t,w}}{A} \tag{2}$$

where, $N_{t,w}$ is total molar gas permeation rate (mol s^{-1}), Δp is the trans membrane pressure difference across the membrane area A. The total gas permeation rate through the membrane at difference pressure was measured using a bubble flow meter. By plotting nitrogen flux $\left(\frac{J_w}{\Delta p}\right)$ as a function of mean pressure $\bar{p}$, the effective surface porosity over pore length was calculated from the slope(S_0) and intercept (I_0) as follows:

$$r = \frac{16}{3}\left(\frac{S_0}{I_0}\right)\left(\frac{8RT}{\pi M}\right)^{0.5}\mu \tag{3}$$

$$\frac{\varepsilon}{L_p} = \frac{8\mu RTS_0}{r^2} \tag{4}$$

The overall membrane porosity was calculated from the ratio of the pore volume to the total volume of the membrane. The membrane pore volume was determined by measuring the increment on the membrane mass before and after being fully impregnated with butanol. The porosity of the membrane was calculated as follows [42],

$$\varepsilon = \frac{V_p}{V_m} \tag{5}$$

where V_p and V_m are the pore volume and total volume of the membrane respectively and average results for both unmodified and the best performing membrane has been reported.

Surface hydrophobicity of the membrane was estimated by contact angle measurements. Water droplets (measured volume of about 2μL) were dropped on membrane surface using Hamilton micro-syringe (0–10 μL) on both modified and unmodified membranes. Droplet position was recorded using a stage mounted video camera. Minimum of five reading were recorded and average contact angle measurements are reported.

2.4. Experimental setup

The schematic membrane distillation experimental setup is shown in Fig. 1. Typical setup consisted of PTFE membrane cell having an effective membrane area of 14.5 cm^2, Viton O-rings, PTFE tubing, PFA and PTFE connectors, feed and permeate flow pump. Constant temperature heating water bath (Neslab Water Bath Model GP 200, NE-SLAB Instruments, Inc., Newington, NH, USA) was used to maintain constant feed temperature and a low temperature bench top chiller unit (Polyscience LS5, Cole-Parmer, USA) was used to maintain the permeate temperature between 15 and 20 °C. Feed and permeate solutions were circulated in a cross flow mode. Both feed and permeate flow passing through the membrane modules were recycled from their respective reservoirs using peristaltic pumps (Cole-Parmer, USA). The inlet and outlet membrane temperatures were monitored using temperatures control probes (Four-channel Data Logging Thermometer, RS-232, Cole-Parmer, USA).

3. Results and discussion

3.1. Membrane characterization

Table 1 presents the different membranes that were fabricated, their characteristics and surface PVDF composition estimated from EDX analysis. The atomic weight percent of fluorine on the membrane