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Enhanced osmotic energy generation from salinity gradients by modifying thin film composite membranes

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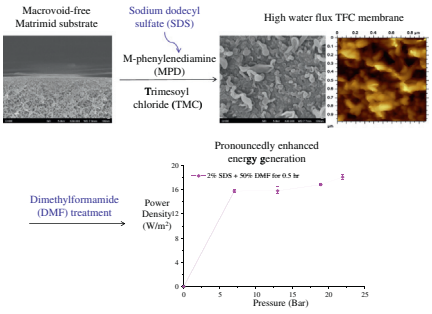
HIGHLIGHTS

- Modified thin film composite (TFC) membrane can sustain 22 bar in PRO process.
- Sodium dodecyl sulfate modification increases free volume intensity of TFC layer.
- N,N-dimethylformamide treatment dissolves less crosslinked parts of the TFC layer.
- With both treatments, the membrane harvests superior energy generation in PRO process.

GRAPHICAL ABSTRACT



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ABSTRACT

Renewable osmotic energy from salinity gradients can be harvested from pressure retarded osmosis (PRO) processes. However, more effective PRO membranes with high power density and pressure resistance are needed to commercialize PRO technologies. In this study, we fabricated thin-film composite (TFC) membranes consisting of a polyamide thin film layer via interfacial polymerization (IP) and a macrovoid-free polyimide support. Three different treatments were explored to improve water flux as well as power density. Firstly, a surfactant of sodium dodecyl sulfate (SDS) was added into the amine IP solution. It resulted in an increase in power density from 8.65 W/m^2 of the pristine membrane to 15.79 W/m^2 of the modified one. Data from positron annihilation spectroscopy (PAS) for the first time confirmed that SDS significantly affected the thin film formation and thus led to a higher power density. The second treatment was conducted by immersing the TFC membranes in N,N-dimethylformamide (DMF) that resulted in a further increase in power density to 16.87 W/m^2. Finally, a combination of both pre- and post-treatments on TFC membranes synergistically enhanced the harvested power density to 18.09 W/m^2, which surpasses all flat-sheet PRO membranes reported in literatures. In addition, the proposed treatments did not sacrifice the robustness of the membranes as they were able to withstand a trans-membrane hydraulic pressure of 22 bar. The newly developed membranes with such mechanical robustness and power density show great potential to practically harvest osmotic power through salinity gradients.

1. Introduction

Energy security is a global issue due to the explosion of population and over exploitation of fossil fuel [1,2]. Meanwhile, sustainable and renewable energy sources are in high demand because of global warming. The osmotic energy harvested from the salinity gradient between seawater and fresh water as electricity [3] has recently received worldwide attention due to its sustainability and environmental-friendliness with great energy potential [4]. Ideally, around 0.8 kW energy can be extracted when one cubic meter of fresh water mixed with seawater [5]. If the retentate of

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reverse osmosis (RO) plants is used as a replacement of seawater, more energy can be generated. In addition, it eliminates the disposal issue of environmental-unfriendly RO retentate [6].

The term of "pressure retarded osmosis (PRO)" was firstly proposed by Loeb in 1975 [7,8]. Basically, it harvests the salinity-gradient energy by allowing water transport from a low osmotic pressure side (i.e., the feed solution) to a high osmotic pressure side (i.e., the draw solution) through a semi-permeable membrane naturally. Since the compartment of the draw solution (i.e., seawater) has a fixed volume, its hydraulic pressure increases with the additional water inflow. As water continuously flows in, this pressure is further raised enough to drive a turbine to generate electricity. According to the prototype design by Statkraft, the power density acquired from flat membranes must be equal or great than 5 W/m^2 in order to have commercial values for PRO applications [9,10].

However, the current PRO technology is hindered by the lack of suitable semi-permeable membranes that have desirable power output [6,9,11–13]. The ideal PRO membrane should have a high water permeability, a low salt permeability and robust mechanical strength to withstand high pressures [6,9,12,14,15]. So far, the thin film composite (TFC) polyamide membranes fabricated via interfacial polymerization (IP) exhibit promising potential. For the development of flat-sheet PRO membranes, some advancements have been achieved. Zhang et al. [16] fabricated TFC flat-sheet membranes on polyacrylonitrile supports with different post-treatments. They reported a power density of 2.6 W/m^2 at 10 bar using 3.5 wt% NaCl as the draw solution. Li et al. [12] fabricated TFC membranes on Torlon substrates with various morphology and compared their structural deformation under high-pressure PRO tests. They also modified the membranes with the aid of pre-compression, polydopamine and chlorine as well as alcohol treatments. The resultant membranes were able to withstand 12 bar and harvested a power density of 2.84 W/m^2 using seawater and de-ionized water as feeds. Achilli et al. [17] studied flat-sheet cellulose triacetate (CTA) FO membranes and obtained power densities of 2.7 and 5.1 W/m^2 respectively using 35 and 60 g/L NaCl as draw solutions. Meanwhile, the effects of internal and external concentration polarization (ICP and ECP) were explored. Li et al. [18] further modified the free volume of TFC membranes by incorporating a bulky monomer into the interfacial polymerization followed by a methanol treatment, their membranes can harvest a power density of 6 W/m^2 and withstand 9 bar using 1 M NaCl as the draw solution. Song et al. [19] fabricated TFC membranes on nano-fiber fabrics and obtained a power density of 15. 4 W/m^2 at 15.2 bar by employing 1.06 M NaCl and 0.9 mM NaCl as feeds, while Han et al. [9] synthesized TFC membranes on macrovoid-free Matrimid substrates which can withstand 15 bar and display a power density of 12 W/m^2 using 1 M NaCl as the feed.

For the development of hollow fiber PRO membranes, Chou et al. [20] developed a TFC hollow fiber membrane on a polyethersulfone (PES) substrate which can harvest a power density of 10.6 W/m^2 using seawater brine and wastewater brine as feeds. However, the membrane can only withstand a trans-membrane pressure of 9 bar. Han et al. [14] fabricated TFC hollow fiber membranes with enhanced mechanical properties and water permeability. Their membrane can produce a power density of 14 W/m^2 at 16 bar from seawater brine and river water. Recently, Zhang et al. [15] synthesized TFC hollow fiber membranes on specially designed PES substrates. The resultant membrane with the minimal salt permeability can harvest a power density of 24.3 W/m^2 and withstand a hydraulic pressure of 20 bar using 1 M NaCl as the feed.

Since the power density of current state-of-art flat-sheet membranes is much lower than that of hollow fiber membranes and more energy loss would be encountered when using flat-sheet membranes in PRO processes due to the flow friction across spacers [21–23], one must further enhance the PRO performance of flat-sheet TFC membranes. Other design and modification strategies should be explored. Surfactants have been reported to improve the formation of the interfacially polymerized layer of TFC membranes [24–26]. Mansourpanah et al. [24,25] added the surfactants into the organic phase as well as the aqueous phase to fabricate TFC nanofiltration (NF) membranes. They found that there were a change in membrane morphology and an improvement on NF performance. This was due to the fact that the amphiphilicity of surfactants acts as a pre-wetting agent that allows a better contact between the amine solution and the hydrophobic substrate [27]. Moreover, the presence of surfactants in the aqueous phase will influence the diffusion of amine into the organic phase. A similar study using polyethylene glycol (PEG) as an additive in amine solutions has also been reported [28]. Hence, we added sodium dodecyl sulfate (SDS) as a surfactant to the amine aqueous solution prior to the interfacial polymerization reaction. In addition to study the SDS influences on FO and PRO performance of TFC membranes, we aim to examine its effects on membrane morphology and other physicochemical properties.

Many chemical and physical modification methods have been proposed on the TFC membrane to enhance its performance. The organic solvent treatment method involves the use of solvents but some of these solvents cause membrane morphological changes permanently [29]. Alcohols are considered to be good treatment agents for polyamide membranes because a higher water flux and a higher power density have been reported [16]. This was due to the fact that alcohols swollen up the membranes and washed away some of low molecular fragments; hence, additional free volumes were generated [16,30]. However, alcohols are not the best solvents to dissolve the polyamide fragments. According to the solubility parameter [29], some stronger polar aprotic solvents such as N,N-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) are more suitable for polyamide membranes. Solomon et al. [29,31] reported a new generation of TFC membranes for organic solvent nanofiltration (OSN) fabricated via interfacial polymerization. The membranes possessed high water permeability without compromising rejection after the DMF, DMSO, etc. treatment.

In this study, mechanically robust macrovoid-free Matrimid membranes were employed as the support substrate for the formation of TFC flat sheet membranes via interfacial polymerization. Since we aimed to enhance TFC membrane performance, the IP selective layer was firstly synthesized with the addition of SDS into the amine aqueous solution at various concentrations and/or the freshly fabricated TFC membrane was post-treated by the DMF solution at various conditions. The physicochemical changes of TFC membranes and their effects on FO and PRO performance were systematically analyzed with the aid of advanced analytic tools. Since positively results on membrane performance and power density have been observed, we believe that this study would offer some inspirations to design suitable PRO membranes for osmotic power generation in the near future.

2. Materials and methods

2.1. Materials

The commercially available polyimide polymer, Matrimid® 5218 (Vantico Inc.) was utilized to fabricate the membrane substrate. The solvent N-methyl-2-pyrrolidinone (NMP, >99.5%) and the non-solvent polyethylene glycol 400 (PEG 400, M_w = 400 g/mol) were purchased from Merck. M-phenylenediamine (MPD, >99%) and trimesoyl chloride (TMC, >98%) were ordered from Sigma–Aldrich and used as the monomers for the interfacial