Title: Robust Membrane for Treatment of Flue-gas Desulfurization (FGD) Waste Water
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Co PI Name: Jason Ren, Rong Long

Research Objective(s):

Our research objective for this seed grant is to develop a new type of robust membrane that can treat challenging waste waters such as FGD water. More specifically, our idea is to develop a new antifouling microporous membrane with controlled surface patterns on both surfaces, which can enhance the mass and heat transfer near the boundary layers in membrane distillation (MD) process of treating FGD water.

The electricity industry is second only to agriculture as the largest domestic user of water, accounting for 39% of all freshwater withdrawals in the nation. The recovery of usable water from powerplant wastewater sources such as FGD waste water, is of great interest. However, the FGD effluent, even after pretreatment steps, contains total dissolved salt (TDS) ranging from 25,000 to 45,000 mg/L. Such high salinity, coupled with the 50 ^{o}C - 60 ^{o}C temperature, makes FGD wastewater difficult to treat using traditional membrane-based desalination technologies. In contrast, MD is ideal to treat such warm, high TDS waste water. Most existing MD membranes suffer from permeation loss due to severe scaling and brine leakage. This is particularly severe when MD process is operated under high water recovery and produces high-salinity hot concentrates. This proposal seed grant offers a new robust membrane to addresses this challenge. The proposal work is highly relevant to the WEN IRT because it addresses a major water treatment challenge for electrical power plant.

Research Activities/Methodology:

The research plan was to establish a fabrication strategy that can impart micron-scale surface patterns on both surfaces of hydrophobic (e.g. PVDF) microporous membranes. Currently, such membranes have not been reported. Established patterning methods such as solvent-induced phase inversion or nanoimprint lithography (NIL) are not applicable to MD membranes. Therefore, most of our efforts under the support of the seed grant are focused on developing a reliable and scalable fabrication strategy. Specifically, we plan to use lithographically templated, thermally induced phase separation (*lt*-TIPS) method to achieve this goal.

Using the seed grant support, one M.S. student (Shouhong Fan, from MSE program) has been making significant progress in this project. His major research activities include.

(a) Identifying suitable chemical/polymer systems for the *lt*-TIPS process. We decided to use PVDF as the polymer for membrane formation. Through extensive literature survey and experimentations in the lab with different high-boiling solvents, tributyl O-acetyl citrate (ATBC) was chosen as the most suitable solvent to use in this study.
(b) The phase diagram of PVDF (MW: 37 kg/mol) /ATBC was established in the lab using the cloud point method with Optical Microscope (OM) couple with a hot-stage.
(c) Flat PVDF membranes were casted through TIPS process, using three different PVDF/ATBC compositions, 15%, 20% and 30 wt% PVDF. These are the control samples that will be directly compared with the patterned counterparts.

(d) Established the fabrication procedure for patterned PVDF. The major steps include: (1) fabricating PDMS mold containing sharklet pattern; (2) preparing PVDF/ATBC solutions at 220 ^oC for 30 min; (3) Degassing the PVDF/ATBC solution at 220 ^oC under vacuum; (4) Casting PVDF/ATBC solution onto pre-heated PDMS mold; (5) Capping the solution with another PDMS mold on the top surface; (6) Cooling the confined solution to induce phase separation between PVDF and ATBC; (7) Removing both PDMS molds and leaching the ATBC out of the membrane using ethanol.

(e) Characterizing the microstructures via SEM, and characterize initial membrane performance via permeation.

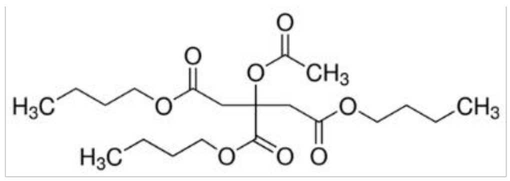
After several months of optimization, Shouhong can now reliably fabricate microporous PVDF with sharklet pattern on both surfaces. Note that this is a significant accomplishment given that no patterned PVDF membrane has ever been achieved, and the process involves high temperature process of organic solvents.

Results:

1. Phase behavior of PVDF/ATBC through cloud point measurement

Figure 1 shows represented OM images of PVDF/ATBC at high temperature (after mixing and degassing) and low temperature (where phase separation occurs). In this specific sample (15% PVDF), spinodal decomposition is observed.

PVDF



ATBC

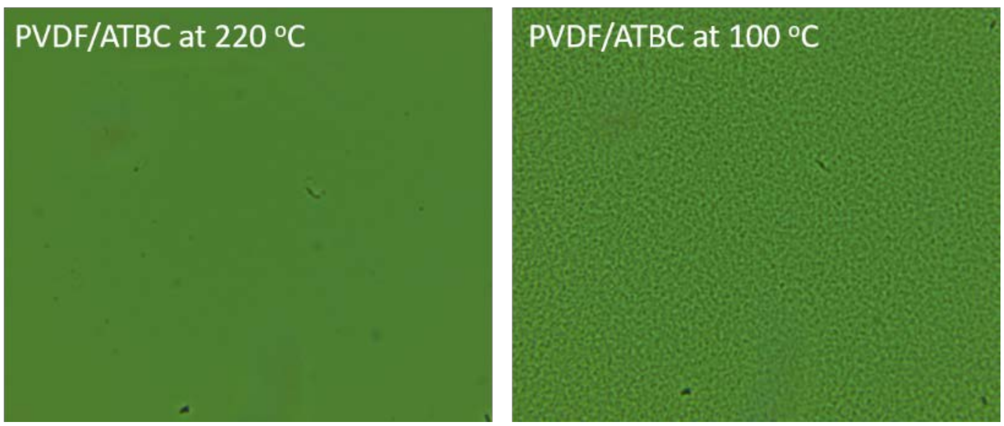


Figure 1. Molecular formula of PVDF and ATBC. OM image of PVDF/ATBC with 15% PVDF at 220 ^oC (left) and 100 ^oC (right) showing the spinodal decomposition pattern.

2. Microstructures of PVDF membranes fabricated

A series of flat-sheet PVDF membranes have been fabricated as control samples using 20%, 30% PVDF/ATBC solutions. Figure 2a and 2b show the cross-sectional SEM images of the fabricated flat-sheet membranes using 30% PVDF.

The most significant results are shown in Fig. 2c and 2d. Sharklet pattern (a commercially available pattern design that mimics sharkskin pattern, which has been shown highly effective at reduce biofouling) has been successfully imparted onto microporous PVDF membranes using the 7-step fabrication procedure described above. The concentration of PVDF/ATBC was 30%. From the high-resolution image (Fig. 2d), the surface pores remain together with the surface patterns. On the back-side of the membrane, similar patterns were also replicated (image not shown here). When 20% PVDF/ATBC was used, the pattern formation was successful, but the uniformity of the pattern was lower than the 30% solution. In comparison, 15% PVDF/ATBC did not produce quality surface patterns, presumably due to the entrapment of ATBC in the mold due to the higher volume fraction of solvent.

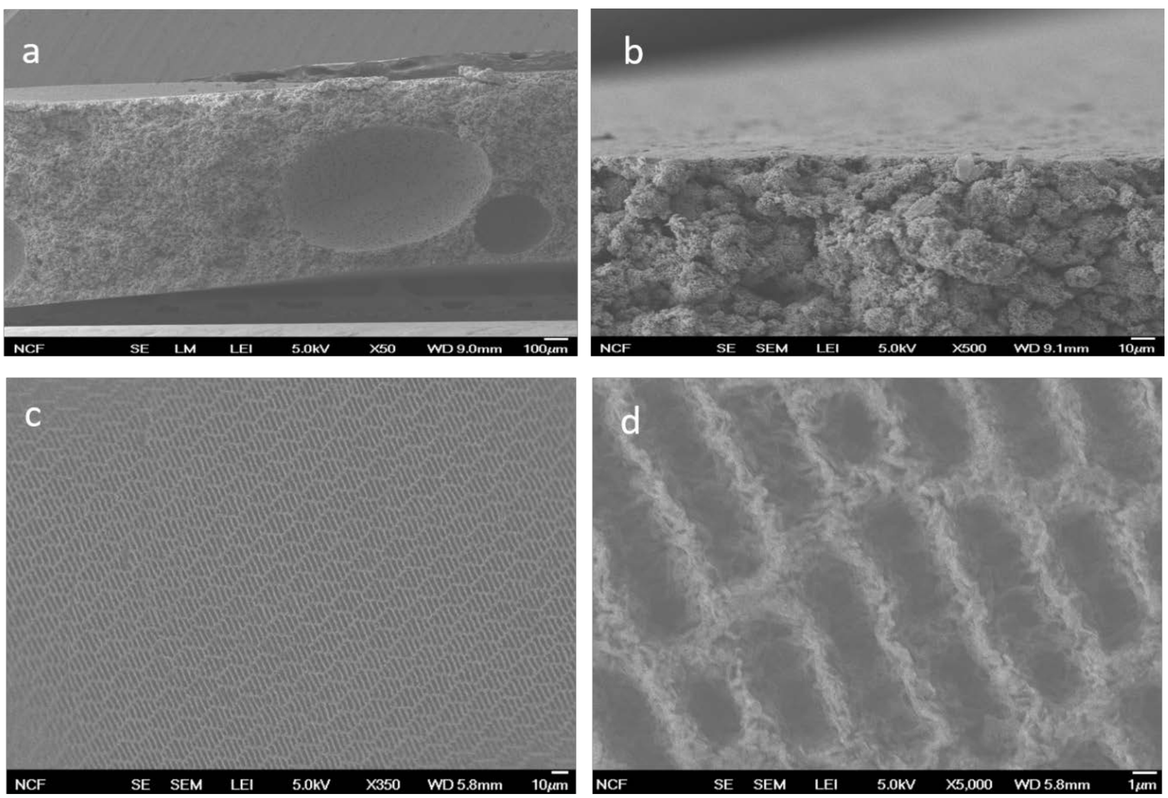


Figure 2. SEM images of PVDF membranes fabricated. (a) Cross-sectional view of PVDF membrane showing large macrovoids. (b) SEM image of cross-section near the surface for the same membrane shown in (a). (c) PVDF membrane with skarklet pattern and its high-resolution view (d).

3. Thermomechanical properties and permselective properties of the membranes

We are characterizing the mechanical properties of these membranes through tensile test. We are also determining the thermal transition temperature (T_g and T_m) of the PVDF in the membranes by DMA. Some preliminary permeation test of the membranes are also being carried out. Figure 3 shows an representative DI water flux over 30 min permeation, showing an average flux of ~68 LMH under a transmembrane pressure (TMP) of 40 psi. It is interesting that membrane showed severe flux decline over 30 min (in the absence of fouling). This is likely caused by the presence of PVDF particles that are not strongly attached to the membrane matrix. This suggests that some post-fabrication process (e.g. thermal annealing) might be necessary to improve the flux of the membrane.

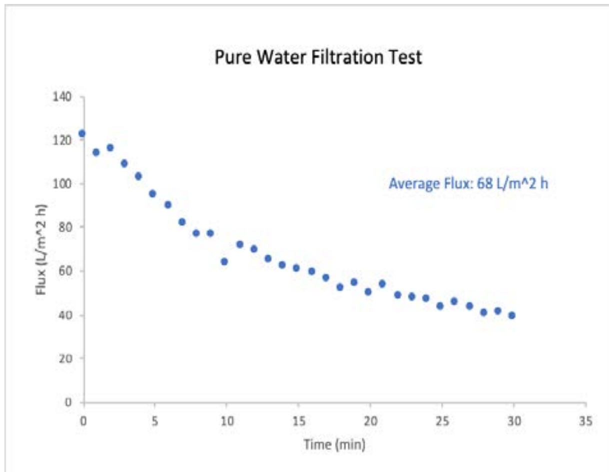


Figure 3. Flux of DI water permeation under a transmembrane pressure of 40 psi, through a flat-sheet PVDF membrane fabricated using 30% PVDF/ATBC.

Accomplishments:

The results achieved above will be published in a high-impact journal once the MD experiments have been completed. We have submitted two grants to DOE (one declined, and one is pending, "Robust Membranes for Efficient Treatment of Power Plant Waste Water", DOE, $400,000 from DOE). We are in process of submitting a MAST center proposal (due April 10th).

Conclusions/Next Steps:

The main outcome of the seed grant project is that we have developed a reliable fabrication method for fabricating surface-patterned MD membranes. Proof-of-concept data (Fig. 2 and 3) that show uniform pattern formation on membranes. In the next stage, we will further characterize the properties and especially the performance of the membranes in MD process. To achieve that, we will need fabricate membranes with area large enough for MD study. Our current area of membrane is typically 4 cm x 4 cm, which is smaller than typical MD cells used.

From funding aspect, we will pursue collaborations that can enhance the MD studies using such membranes. This has becoming an issue since Jason Ren has left CU. Our current plan is to work with Prof. Tong from CSU (a MD process expert). We will prepare proposals to MAST center, US Bureau of Reclamation, DOE, and NSF.