Scalable Manufacturing of Layer-by-Layer Membranes for Water Purification

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“When the well is dry, we know the worth of water.” – Benjamin Franklin.

Water is critical to the health and security of our nation. This was highlighted recently when the Obama Administration hosted the White House Water Summit to raise awareness of water availability issues across the U.S. and to engage stake-holders in identifying long-term solutions for water production and management to invest in. Water availability is not a new issue – the demand for clean water has risen dramatically since the arrival of the Industrial Revolution and will continue through the Information Age and beyond. During these eras, the world’s population has climbed to 7 billion, and as this population continues to expand and water scarcity becomes a reality, we as a people need to think creatively on how we safeguard access to clean water. The obvious and most fundamental purpose of clean water is as a source for sustenance, to produce the food and water that we as a society need to survive. But clean water is also vital to many of the complex processes that produce the technology that our society demands and consumes. Consequently, many of those processes also introduce contaminants to our water supplies, such as heavy metals and other chemicals. Therefore, there is a clear and growing need for technologies and processes that ensure the water we rely on every day is clean, safe and accessible [Shannon et al. 2008].

Membranes and membrane technology are key components to the world’s water future, in particular polymer-based membranes [Geise et al. 2010]. Membranes are capable of separating a wide range of contaminants from impaired water sources, from viruses and bacteria to heavy metals to dissolved salts. Given that water covers 71% of the Earth's surface and 97% of that water can be found in the world's oceans, an obvious focal point of our attention has been given to desalination, or removing water from high salinity water sources. This can be an energy intensive process due to the high osmotic pressure of sea water – the average sea-surface salinity is 35,000 g/L (for simplicity, let's assume it is all sodium chloride), which generates an osmotic pressure ($\Delta\pi$) of nearly 400 psi or 27.4 bar. Even so, desalination remains highly attractive due to the volume of water available for recovery. This presentation will focus primarily on membrane desalination via reverse osmosis, so a short introduction to reverse osmosis is warranted.

In traditional osmosis, water flows across a semi-permeable membrane from regions of low solute concentrations (in this example, pure water) to regions of high solute concentration (a concentrated salt solution), in effect diluting the solute and lowering the overall free energy of the system. The driving force for the flow of water is the osmotic pressure ($\Delta\pi$) and is a dependent on the concentration of solute molecules in the concentrated solution. In reverse osmosis, pressure is applied to the high concentration region, which has to be greater than the osmotic pressure of the solution, to drive water from regions of high concentration to regions of low concentration (see Figure 1), again with the aid of a semi-permeable membrane. This process generates purified water on one side of the membrane and a more concentrated salt solution on the other side.

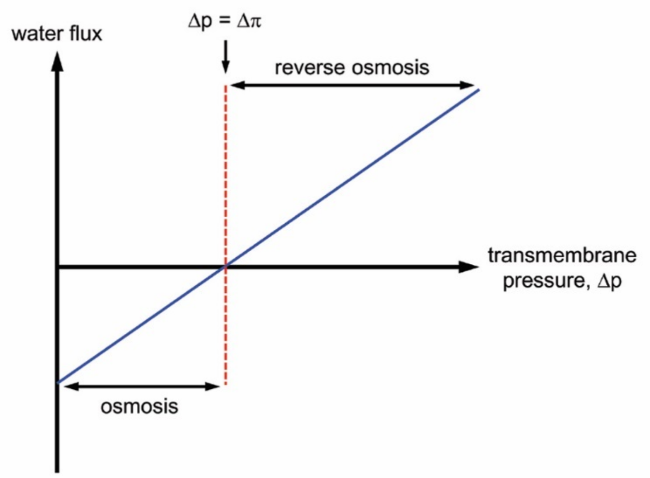

FIGURE 1. Schematic diagram of water flux as a function of applied pressure, indicating the regimes for traditional osmosis ($\Delta p < \Delta\pi$) and reverse osmosis ($\Delta p > \Delta\pi$).

The water flux (J_w) through the semi-permeable membrane can be defined as:

$$J_w = A\frac{K_w}{h}(\Delta P - \Delta\pi)$$

where A is the membrane area, K_w is the permeability of the membrane, h is the membrane thickness, and $(\Delta P - \Delta\pi)$ is the difference between the applied pressure and the osmotic pressure. From this equation, one can see that there is an inverse relationship between the applied pressure and the membrane thickness. Thus, a thinner membrane would be ideal as it would require less energy (pressure) to generate a given amount of water.

The manufacturing of today's state-of-the-art reverse osmosis membranes is based on 1970's technology of interfacial polymerization of the selective layer directly a porous support [Cadotte 1977; Cadotte 1979]. In this process, polymerization of an aromatic triacid chloride (A) and an aromatic diamine (B) occurs at the interface of two immiscible liquids, where one liquid (typically the aqueous amine solution) is wicked into the porous support. The result is a highly crosslinked, aromatic polyamide (think crosslinked Kevlar or Nomex) membrane that selectively allows the passage of water and rejects salt. The chemistry easily lends itself to roll-to-roll (R2R) or web processing, can be performed over large widths of substrates, and produces a relatively low number of defects across the membrane surface. Over the next 40 years, this membrane technology has slowly evolved through an Edisonian, trial-and-error approach. The process makes extremely thin (100’s nm) selective membranes, but these membranes are difficult to characterize due to high roughness and large heterogeneity. Thus, our fundamental understanding of how these membranes work is insufficient to allow the rational design of next-generation membranes. In 2011, we proposed a paradigm shift in how these types of membranes are fabricated, where the selective layer is created layer-by-layer through a reactive deposition process. By doing so, we anticipated the membranes to be smooth, tailorable, and exceptionally thin (10’s of nm). The ability to tune the membrane thickness makes this process attractive due to potential energy savings from reduced pressure requirements.

In our original demonstration [Johnson et al., 2012], we employed a solution-based deposition process where we sequentially and repeatedly layered each reactive monomer (A + B) onto a solid substrate. We observed growth rates of approximately 0.34 nm/cycle, where one cycle represents a single (A + B) deposition sequence. The growth rate was shown to be dependent on monomer chemistry, spin conditions, and rinse solvents [Chan et al. 2012]. Additionally, the layer-by-layer films are quite smooth, exhibiting a root mean square (RMS) roughness of 2 nm compared to commercial interfacial polymerized membranes that exhibit an RMS roughness of 100 nm or more. The fact that the films are relatively smooth and homogeneous has two compelling advantages: 1) it enables advanced measurements of the film structure via scattering- or reflectivity-based techniques, among others, and 2) it allows *quantitative* structure-property relationships to be developed as the film thickness, h, is well defined. X-ray photoelectron spectroscopy and swelling measurements indicate that the crosslink density of the layer-by-layer membranes is comparable to their commercial counterparts, even though the layer-by-layer films are considerable thinner [Chan et al. 2013]. Additionally, other researchers have adopted this approach and verified that membranes produced using this layer-by-layer process indeed have viable water flux and salt rejection [Gu et al. 2013].

One major drawback to the solution-based layer-by-layer approach is throughput – spin-assisted assembly is a relatively slow process and is not easily scalable. Recently, we have started to explore the use of a vapor-based approach where each monomer is deposited in the gas phase, similar to atomic layer deposition of metals and oxides. In this embodiment, each monomer/precursor is heated in order to build up sufficient vapor pressure of the precursor. Each monomer is then metered into a rotating drum reactor with nitrogen sweep gas and differential pumping on either side (see Figure 2), and again the number of cycles (or number of consecutive ports) determines the thickness of the resulting membrane. This approach has many advantages over the solution-based approach, such as speed, safety, and scalability. We have shown that we can deposit 20 layers of (A + B) per minute (5 s/cycle), compared to 1 layer of (A + B) every 2 minutes using the solution-based approach (2 min/cycle). The growth rate using the vapor-based approach (0.36 nm/cycle) is nearly identical to the solution-based approach, ensuring that the processes are similar. One key advantage of the vapor-based

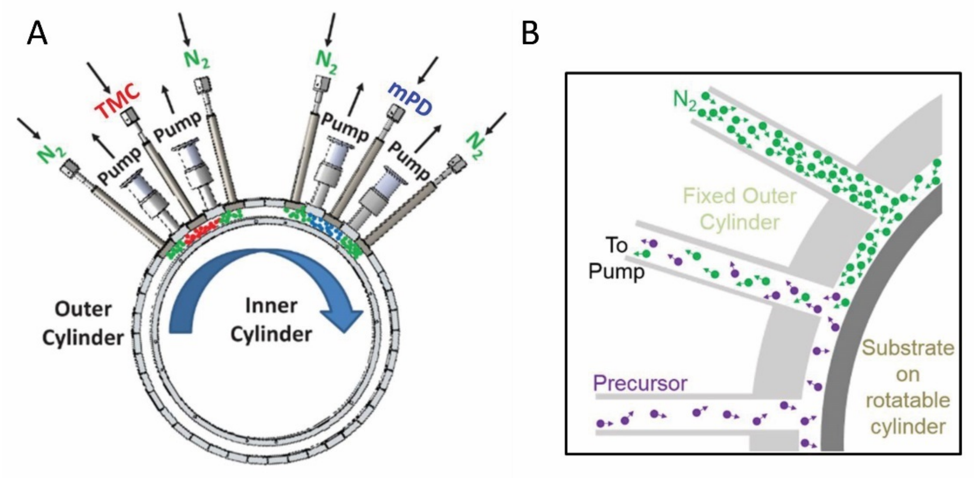

FIGURE 2. A) Schematic of a spatial molecular layer deposition reactor for the alternating deposition of reactive monomers/precursors to form polyamide membranes. B) Zoomed in view of monomer/precursor arrival to the rotating/moving substrate and removal of unreacted monomer/precursor by the sweep gas and pumping.

approach is the potential for scale-up via continuous, roll-to-roll (R2R) or web processing. But there are still many challenges yet to overcome, from membrane support design to membrane characterization. The current state of research in the area of polyamide membranes produced via layer-by-layer deposition will be discussed, and the opportunities and challenges in scalable, R2R manufacturing of these types of membranes will be assessed. Such a paradigm shift in manufacturing may lead to more energy efficient membranes and processes, offering one solution to the grand challenge of water security.

Further Reading

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