



ENERGY RESEARCH AND DEVELOPMENT DIVISION

FINAL PROJECT REPORT

Water Recovery Desalination of Non-Traditional Waters

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PREFACE

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ABSTRACT

This research describes the design of new materials and research into sustainable membrane treatment practices to reduce the energy demands of water purification processes, including inland desalination. These technologies can help California reach its sustainability goals for water treatment, by considering the energy demands required by advanced water treatment and targeting plant inefficiencies caused by fouling and redundant process requirements of traditional materials. Brine disposal, membrane fouling, and membranes' sensitivity to chemical treatment contribute to high energy costs associated with membrane-based water treatment by increasing the pressure required for membrane operations or by causing the need for additional pre-treatment and/or post-treatment steps. This work addresses these problems by applying materials science. In particular, the research studied ways to modify commercial membranes to prevent membrane fouling and examined methods to make membranes that are highly chemically tolerant and can be tailored selectively. The research also reviewed existing technologies for the sustainable operation of membrane treatment facilities. A single-step process was developed for the photochemical treatment of commercial membranes to create hydrophilic surfaces that resist fouling by preventing surface adhesion of hydrophobic foulants and preventing biofilm propagation on membrane surfaces. Addressing the chemical intolerance of the materials used commercially to fabricate membranes, the research team developed a method for making composite membranes from materials with enhanced properties including chemical tolerance. These approaches were designed with scalability in mind. A roll-to-roll prototype was built for the photochemical modification of membranes, while robust chemistries and scalable methods were used and developed for each of the novel membrane designs. By focusing on specific problems and scalable methods, this research brings new solutions closer to real-world applications. Simulated water treatment scenarios suggest that these materials offer new ways to overcome common membrane treatment challenges.

Keywords: antifouling, anti-scaling, desalination, hydrophilicity, membranes, water treatment

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Executive Summary

Introduction

Water scarcity in California is widespread and made more unpredictable due to climate change. Often, urban centers are largely dependent on imported water, which disrupts ecosystems and requires a significant energy cost for the transport of water. The dividing up of surface water for agriculture and the quality of runoff from different agricultural sites can negatively impact different crops as well as have damaging effects on the groundwater sources that are recharged by the runoff. For these reasons and others, alternative sources of water are becoming increasingly attractive throughout the state.

Membrane filtration is the most energy efficient way of removing salt and other chemicals from water — the types of pollutants that deem many water sources unusable for potable, agricultural, or even industrial uses. While membrane technology brings with it many opportunities, using it for recycling wastewater, desalinating ocean water, or desalinating groundwater has a significant energy footprint and requires large capital investments in both water treatment infrastructure and energy systems to support infrastructure operation. After capital costs, the cost of desalinated water is then dependent on the cost of energy.

Stresses on available freshwater resources will soon require the use of non-traditional waters such as brackish groundwater and municipal wastewater as essential solutions to current water supply problems. These non-traditional waters commonly contain considerable amounts of impurities, which must be removed by appropriate treatments before the waters are supplied to end-use customers. In most cases, the impurities include an array of salt ions (for example, sodium, potassium, calcium, chlorine, carbonate, beryllium nitrate, and sulfate). Many industrial and municipal applications cannot tolerate even small concentrations of these salt ions in the supplied water. Due to its competitive energy consumption and water production costs, membrane-based desalination such as reverse osmosis is one of the most commercially important methods for removing salts from water. Because most commercial desalination processes achieve salt removal by separating clean water from impure water, the processes typically produce a wastewater stream with high salt concentrations, called either brine or concentrate.

To take advantage of the possibilities that more widespread use of membrane treatment offers, one must address how the additional treatment capacity fits into the context of California's energy policies and goals. For now, these problems are not often addressed because traditional sources of fresh water, primarily surface water, are much cheaper than highly treated, recycled water. While catalyzed by the rising cost of water in California, getting to a more competitive point, where desalination has similar costs to surface water, will require capital investment, consumer acceptance, and policy enactments.

Water recovery from desalination is a key factor in determining the quantity and quality of the concentrate. As the desalination process recovers pure water from impure feed water, the concentrate stream contains higher salt concentrations in lower discharge volumes. In inland and arid areas far from the sea where it is extremely difficult to properly dispose of the

concentrate, the operational expenditures for desalination are intensely regulated by the concentrate treatment costs, which are commonly proportional to the discharge amount of the concentrate stream. The ideal desalination process can recover the full amount of pure water from a given water source and discharge no concentrate waste stream. However, such elevated water recovery thermodynamically intensifies the energy demand for water-salt separation and, thus, harms the desalination energy efficiency. To buffer this energy stress of high water recovery on desalination, the conventional desalination process must be improved with either an advanced membrane material or an innovative system design, which would help the desalination process alleviate the thermodynamic limit on the water-salt separation.

Ideally, renewable energy sources would power desalination operations, thus separating the cost of water from the cost of fossil fuels and the production of greenhouse gas emissions. Minimizing the energy and maintenance demands of desalination operations increases the likelihood of adoption of non-traditional sources of water in the regions that need it most. This project addressed different aspects of the reduction of energy requirements for desalination:

- The reduction of energy costs due to membrane fouling and associated cleaning
- The reduction of energy costs by reducing the number of pretreatment steps or the number of times water must pass through a membrane to reach the purity necessary for a particular application
- The compilation of information on membrane processes, their energy requirements, and efforts to make desalination more sustainable for ease of understanding and access across disciplines

Fouling and brine disposal are two major contributors to the energy intensity of desalination. Fouling is the accumulation of biological material or minerals on the surface of membranes that makes it more difficult to push water through the membranes to produce clean water. Brine is the concentrated saline solution left over after water has been treated using membranes.

Project Purpose

The project had three primary purposes:

- 1. Investigate state-of-the-art desalination processes that can enhance water recovery efficiency and reduce the amount of brine discharge.
- 2. Develop a nano-structured membrane that can lower membrane fouling and, thus, energy consumption.
- 3. Assess the technical and cost performances of state-of-the-art concentrate treatment strategies.

The team hoped to create a scalable method for modifying the surfaces of reverse osmosis membranes that would reduce irreversible fouling of membrane surfaces using techniques that are scalable and thus economically feasible for industrial applications. Another goal was the design and manufacture of high-recovery membranes using novel materials.

Project Approach

The most economical approach to reducing the costs due to fouling was not to make membranes out of an entirely new material, but simply to modify membranes that are already commercially available. A surface modification was developed in chemistry labs by undergraduate, graduate, and postdoctoral researchers at the University of California, Los Angeles. The coating was applied to commercial reverse-osmosis membranes and tested using lab-scale, high-pressure filtration units for resistance to fouling and scaling. Adhesion of biological media to surfaces with the coating was performed where bacteria were directly cultured on coated surfaces. A prototype, roll-to-roll coating machine was developed that applied the coating to rolls of polyethylene, a process that is applicable to spiral wound membranes.

Technical barriers were addressed through collaboration across departments. Engineering and chemistry students and postdocs worked together to address experimental and data analysis tasks. A few non-technical barriers were encountered that included usual situations such as student graduation or absence of the principal investigator, that were easily overcome by training new students and assigning managerial tasks to one doctoral student who was present throughout the entire grant period.

Project Results

This research developed a single-step process for the photochemical treatment of commercial membranes to create hydrophilic surfaces that resist fouling by preventing surface adhesion of hydrophobic foulants and preventing biofilm propagation on membrane surfaces. A roll-to-roll prototype was built for the photochemical modification of membranes, while robust chemistries and scalable methods were used and developed for each of the novel membrane designs. By focusing on specific problems and scalable methods, this research brings new solutions closer to real-world applications. Simulated water treatment scenarios suggest that these materials offer new ways to overcome common membrane treatment challenges.

Regarding the goal to reduce energy consumption in the desalination process, the primary way to reduce the emissions is to reduce the amount of energy consumed and/or transition to renewable energy resources. State policies regarding the amount of waste generated by plants are one way to incentivize technology adaptation. Similarly, state incentive programs to make buildings and facilities carbon neutral may also increase the likelihood of adoption of low-fouling membranes in water treatment facilities.

A reduction in operation expenditure may further stimulate the market for inland desalination and membrane purification facilities. While membrane technology has advanced dramatically in recent decades, it has also become much cheaper to make high-efficiency membranes. The cost of adding a step to the manufacturing of standard spiral-wound membranes needs to be smaller than the increase in operating expenditure due to fouling.

Advancing the Research to Market

The team's basic research findings on coatings have been published in academic journals and have, during the past six years, received more than 120 citations. Long-term target markets are membrane manufacturers that could integrate the roll-to-roll process into their spiral-

wound membrane module fabrication. Potential uses for membrane coatings developed in this research may also have implications for uses in other industries such as the medical and food and beverage industries.

Benefits to California

California has strict policies regarding desalination and reuse. By improving membrane technology and reducing energy usage for desalination, this research can improve access to sustainable sources of fresh water through the treatment of brackish water and can contribute to improving the energy efficiency of technologies that will make California more water-independent. Reducing the impact of fouling may reduce the treatment facilities' operating expenses and reduce capital expenditures needed in pre-treatment steps to protect and extend the lifetime of membrane modules.

CHAPTER 1: Introduction

Setting the Stage for Inland Desalination in California

Water scarcity in California is widespread and made more unpredictable due to climate change. Often, urban centers are largely dependent on imported water, which disrupts ecosystems and requires a significant energy cost for the transport of the water. The division of surface water for agriculture and the quality of runoff from different agricultural sites can negatively impact different crops and have damaging effects on the groundwater sources that are recharged by the runoff. For these reasons and others, alternative sources of water are becoming increasingly attractive throughout the state.

Membrane filtration is the most energy-efficient way of removing salt and other chemicals from water, thus eliminating the types of pollutants that make many water sources unusable for potable, agricultural, or even industrial uses. While membrane technology brings with it many opportunities, using it for recycling wastewater, desalinating ocean water, or desalinating groundwater incurs significant energy footprints and requires large capital investments in both water treatment infrastructure and energy systems to support treatment operation. After capital costs, the cost of desalinated water is then dependent on the cost of energy and thus on the cost of fossil fuels.

Stresses on available freshwater resources will soon require the use of non-traditional waters such as brackish groundwater and municipal wastewater as essential solutions to current water supply problems. These non-traditional waters commonly contain considerable amounts of impurities, which must be removed by appropriate treatments before the waters are supplied to end-use customers. In most cases, the impurities include an array of salt ions such as sodium (Na⁺), potassium (K⁺), calcium (Ca²⁺), chlorine (Cl⁻), carbonate (CO₃²⁻), beryllium nitrate (NO₃²⁻), and sulfate (SO₄²⁻). Many industrial and municipal applications cannot tolerate even small concentrations of these salt ions in the supplied water. Due to its competitive energy consumption and water production costs, membrane-based desalination such as reverse osmosis (RO) is one of the most commercially important methods for removing salts from water. Because most commercial desalination processes achieve salt removal by separating clean water from impure water, the processes typically produce a wastewater stream with high salt concentrations, called either brine or concentrate.

Taking advantage of the possibilities that more widespread use of membrane treatment offers must address how the additional treatment capacity fits in the context of California's energy policies and goals. For now, these problems are not often addressed because traditional sources of fresh water, primarily surface water, are much cheaper than highly treated, recycled water. While catalyzed by the rising cost of water in California, getting to a point where desalination has similar costs to surface water will require not only capital investment but also consumer acceptance and policy adaptations.

Challenges for Inland Desalination

The water recovery from desalination is a key factor in determining the quantity and quality of the concentrate. As the desalination process recovers pure water from impure feed water, the concentrate stream contains higher salt concentrations in lower discharge volumes. In inland and arid areas far from the sea where it is extremely difficult to properly dispose of the concentrate, the operational expenditures for desalination are intensely regulated by the concentrate treatment costs, which are commonly proportional to the discharge amount of the concentrate stream. The ideal desalination process would be able to recover the full amount of pure water from a given water source and discharge no concentrate waste stream. However, such elevated water recovery thermodynamically intensifies the energy demand for water-salt separation and, thus, harms the desalination energy efficiency. To buffer this energy stress of high water recovery on desalination, the conventional desalination process must be improved with either an advanced membrane material or an innovative system design, which would help the desalination process alleviate the thermodynamic limit on the water-salt separation.

Ideally, renewable energy sources would power desalination operations, thus separating the cost of water from the cost of fossil fuels and the production of greenhouse gas emissions. Minimizing the energy and maintenance demands of desalination operations increases the likelihood of adoption of non-traditional sources of water in the regions that need it most. This project has addressed different aspects of the reduction of energy requirements for desalination:

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Specific Membrane Challenges

Membrane technologies for RO depend on how fast water travels through a membrane material compared to whatever is dissolved in the water that one seeks to remove. Additional resistance to water flow can be caused when layers of biological or inorganic material accumulate on the surfaces of membranes as a natural result of the filtration process.

Membrane Fouling

Membrane fouling occurs when bacteria attach to a membrane and generate a biofilm. Biofilms then act as production ground for other bacteria. Normal methods of preventing bacterial growth in water are via chlorination or other chemical disinfection processes. Polyamide, the most commonly used membrane material, is very sensitive to chlorine (Cl) and other chemical treatments.

Membrane Scaling

Membrane scaling is a problem that occurs in all membrane processes where aqueous minerals are in the feed water. As pure water is generated in the permeate, the concentration at the interface of the feed and the membrane becomes highly concentrated and as the solutes reach their solubility limit, they precipitate out of solution onto the membrane. These crystals then act as seeds for further crystal growth on the membrane surface. Methods of scaling reduction include increasing the cross-flow velocity of the system, adding chemical anti-scalants (usually surfactant formulations), and carefully monitoring the pH to avoid ideal saturation conditions. Figure 1 illustrates membrane scaling.

Figure 1: Micro and Macro Scale Images of Membrane Scaling in the Lab



(a) Early-stage scaling on the surface of a brackish water RO membrane. White faceted spots are the initial crystals formed on the membrane surface. (b) Lab-scale membrane test cell with salt buildup and the corresponding, severely scaled, membrane.

Brine Management

Even once fouling is addressed, the need remains to dispose of brine or waste solids safely and sustainably. While advancing materials can help make existing technologies more efficient, choosing the right technology for the treatment of waste concentrates requires evaluation of a wide variety of options available for management; close attention must be paid to the sustainability of each practice.

Chemical Intolerance

The most efficient membranes are often made from materials that are extremely susceptible to degradation by common chemical treatments. For example, Cl in water (a common disinfectant) will destroy many commercial membranes. Therefore, water needs additional pre-treatment to remove all Cl before contacting the membrane or must not be chlorinated. While the lack of chlorination saves the membranes from chemical damage, it also makes it easier for biological material to adhere and grow on the membrane surfaces.

Selectivity

Selectivity describes how well a membrane separates a very particular pollutant. As we turn toward the re-use of increasingly contaminated water, the ability to reliably remove a variety of charged and uncharged pollutants becomes more important than ever. Although membranes exist that are highly selective for sodium chloride (NaCl) and other salts, the solution to removing other pollutants is often increased chemical treatment of water entering and leaving membrane trains or an increased number of passes water makes through a membrane before it can be considered "pure." In either case, this lack of selectivity causes an increase in the energy demand of a membrane process.

CHAPTER 2: Project Approach

Membrane Technology

This project addresses the energy hurdles to inland desalination in two ways: authorship of reviews and experimental/material design.

The purpose of the review authorship is to evaluate state-of-the-art optimization and control strategies for membrane-based desalination systems to achieve higher product water recovery and reduced energy consumption than conventional RO system designs. A book entitled *Sustainable Desalination and Water Reuse* addresses all aspects of reverse-osmosis plant operational costs and the arguments for different types of energy/waste-reduction approaches. This provides a comprehensive and accessible means for stakeholders to learn both the fundamentals of desalination processes and desalination plant operation.

When it comes to designing new materials for membranes that address the need to reduce energy consumption, there are three general approaches:

- (A) Make membranes that foul less.
- (B) Make more chemically robust membranes that can tolerate chemical treatments, eliminating the need for special pre-treatment steps that increase energy and capital costs.
- (C) Make membranes that require fewer filtration steps to remove the solute of interest: more "selective" membranes.

The experimental component of this work took all three approaches. The primary focus was the scalable, surface-modification of membranes to prevent scaling and fouling. The second was the development of a novel platform for asymmetric membrane fabrication that uses highly chemically-tolerant materials. Finally, using the aforementioned platform, the third was the development of membranes tunable to specific applications.

Mitigating Fouling and Scaling of Desalination Membranes

In any membrane process a "feed stream," a water source that contains unwanted solutes in other words "dirty water" — is contacted to a thin piece of plastic called a membrane. The membrane is designed to withstand the pressure of the water being forced through it and to slow down particular solutes more than it slows down water. This can be either by pores that exclude particles of a particular size or by what are called "intermolecular forces" between the solutes in the water and the membrane material. This produces a "permeate stream" that is essentially "clean water," or water in which the concentration of unwanted solutes is greatly reduced. The permeate can either be put through additional membranes to make the water even cleaner or prepared for distribution. Two types of fouling occur in membrane processes: irreversible and reversible. Irreversible fouling permanently damages a membrane by diminishing the membrane materials' integrity. Reversible fouling is easily solved by cleaning membranes. In all membrane processes both processes occur to a particular extent. Where material advancement can come into play is in altering how specific solutes in the feed interact with solutes in the water, not only to slow them down to be separated, but to also prevent any type of permanent attachment to the membrane.

To prevent irreversible fouling of membranes, a technique called perfluorophenylazide (PFPA) photochemistry was used to modify water filtration membrane surfaces due to its simplicity and scalability. With this technique, PFPAs act as molecular-scale anchors. By synthesizing molecules that make surfaces less likely to foul and attaching the PFPA group to them, brief exposure to ultraviolet (UV) light can bind the molecules to nearly any material surface. The portion of the molecule highlighted in green in Figure 2 is the "anchor" portion of the molecule. The part that is not highlighted is customizable and can be designed to encourage or prevent a particular type of interaction with the membrane surface.

Figure 2: Zwitterionic Molecule with PFPA "Anchor"



The PFPA acts as an anchor to a polymer surface. The N3 group, known as an "azide," is highly reactive and binds to surfaces upon exposure to UV radiation.

Figure 3 gives an idea of how these molecules act to prevent fouling. The left image shows how matter in the feed stream can accumulate on the surface of a membrane if the attraction between them is strong. Sometimes this matter is the unwanted solute in the feed stream, or it is organic matter like bacteria that begins to grow on the surfaces of membranes over time. This can clog membrane pores and prevent diffusion through the material. The image on the right shows PFPAs bound to the surface of the material. The black and red portions of the molecule anchor the blue, specially designed portion, to the membrane surface.

Figure 3: PFPA Modification on Membrane Surface Preventing Adhesion of Foulants



Schematic of polyethersulfone (PES) ultrafiltration (UF) membrane with and without PFPA modification. R1 and R2 represent chemical moieties designed to prevent the adhesion of biological material to the membrane surface. The N3 has been converted to a nitrogen (N) bound to the membrane surface.

By synthesizing different kinds of PFPAs, attaching them to a variety of membrane surfaces, and simulating industrial water separation processes in the lab, the research team evaluated the potential for this type of modification to help reduce the energy consumption of membrane processes. Some of the PFPA technology was developed before the beginning of the UC/China Clean Energy Research Center for Water-Energy Technologies/California Energy Commission (CERC-WET/CEC) program and is patented material, while other technologies were developed during the funding period and published in academic journals.

A New Approach to Membrane Design: Thin-Film Liftoff

This next material strategy informs both the second and third approaches, both (B) and (C) mentioned previously. Because membranes are often very sensitive to harsh chemicals used for cleaning membranes and fouling reduction, pre-treatment steps must be included to prepare the water to be contacted with membranes. Additionally, simple measures, such as chlorinating water, to prevent fouling cannot be taken because they will damage the material integrity of the membranes, reducing their efficacy. Therefore, chemically resistant, non-traditional materials have long been investigated as potential alternatives, but are seldom adapted due to production hurdles or reduced compatibility with existing membrane infrastructure.

The third approach (C) has to do with reducing the number of times a saline or otherwise contaminated water source needs to pass through a membrane to remove contaminants. In other words, increasing the "selectivity" of a membrane can create energy savings in ways similar to reducing pre-treatment steps: reducing the actual number of times a permeate stream needs to be filtered.

To facilitate these potential energy advancements, the research team developed a method that allows very robust and often difficult-to-process materials to be used as the selective material in membranes. The team hoped to achieve a degree of simplicity that allowed the

testing of all kinds of membrane materials for selectivity while retaining a general standard of chemical tolerance across all designs. This method is called "thin-film liftoff" or "T-FLO."

In T-FLO, a thin film of "selective" material is cast onto a glass substrate. This material is designed to be chemically tolerant as well as theoretically efficacious for the removal of a particular solute. Epoxy resin, known for its strength and chemical tolerance, is dissolved in a special liquid called a "porogen" and then poured onto the thin film and cured. After porogen removal, a functional "asymmetric" membrane is formed. It is "asymmetric" because the thin film is dense and its role is to remove pollutants, while the epoxy resin portion is porous and is there only to support the thin film during filtration. This process is summarized in Figure 4, while Figure 5 shows the asymmetric structure of a finished T-FLO membrane.



Figure 4: Thin-Film Liftoff Technique for Membrane Fabrication

Thin-film liftoff process: Image of an actual T-FLO membrane after testing in a dead-end filtration run.



Figure 5: Asymmetric Membranes Cross-sectional Images

Cross-sectional images of a membrane made using T-FLO.

Membrane Testing

Once membranes were either modified or fabricated according to either approach, filtration processes were simulated. Simplified feed streams were produced and were pressurized across membranes using specially designed test cells. Experiments were designed to isolate a particular fouling event or separation process. The success of a process or membrane was evaluated by how quickly clean water could be recovered under applied pressure and flux, as well as how well it removed solute from a feed stream by comparing the feed and permeate streams.

CHAPTER 3: Project Results

Review of Desalination Technologies

This chapter explores a range of treatment processes aimed at enhancing RO membranes, with the primary goal of alleviating the challenges associated with brine disposal in inland desalination projects.

PFPA Modification of Reverse Osmosis Membranes

In general, the PFPA molecules in this study endow surfaces with greater hydrophilicity where hydrophilic translates literally as "water-loving." By permanently holding a layer of water at the interface of a wet membrane and a water stream, one can prevent the permanent adhesion of unwanted materials to the surface of membranes. While the team synthesized several types of PFPA molecules, and the possibilities are nearly endless in terms of what one can add to a PFPA anchor, this discussion focuses on the synthesis of three types of PFPA molecules: a small molecule zwitterion, a tetraaniline, and a zwitterion-copolymer.

A zwitterion is a type of molecule that has both a positive and a negative charge that exist on the molecule simultaneously without canceling each other out. The chemical scheme for the synthesis of a zwitterionic PFPA is shown in Figure 6. In the first step, a molecule replaces the sulfur (S) Cl bond on the starting substrate. Then, one of the fluorine atoms is replaced with an azide (N_3) group, making the molecule reactive upon exposure to UV light. Finally, a molecule called a "sultone" is added to the nitrogen (N) atom on the end of the molecule. Notice in the final image that the "N" atom has a positive sign and one of the oxygen atoms at the end of the chain has a negative sign. This is the zwitterionic portion of the PFPA that helps to hold a layer of water next to the membrane.

Figure 6: Three-Step Synthesis of Small-Molecule PFPA



PFPA-small molecule with zwitterion is made in three steps under mild conditions. Source: Rao et al., 2018 Another PFPA is tetraaniline PFPA (Figure 7). The prefix tetra, meaning four, and aniline, a benzine ring with an NH₂ or "amine" group, is an oligomer of the conducting polymer polyaniline. An oligomer is a very short segment of a polymer, which is a very long chain of molecules. Polyaniline has several unique properties that are dependent on the acidity or alkalinity of the water that it is in. It is also known to resist bacterial growth and adhesion. In previous work, the researchers studied the properties of tetraaniline (TANI) in supercapacitors and batteries. Nanostructured polyaniline is now used commercially in membranes developed in the researchers' labs under the trade name "PolyCera[®]." The name PolyCera came from a combination of a material that can be processed like a polymer but has the separation attributes of a ceramic.



Figure 7: Three-Step Synthesis of TANI PFPA

Once TANI is made, PFPA-TANI can be made in three steps.

Source: Lin et al., 2019

The last synthesis shown here is that of the PFPA-zwitterion copolymer. This was inspired by the small-molecule zwitterion shown in Figure 8; but rather than grafting individual zwitterionic groups, alternating chains of PFPA anchors and zwitterionic stretches were made. Then, the PFPA portion of the chains could be activated by UV light, attaching the long chains of zwitterion to a surface. This gave more uniform and continuous coverage of a surface compared to the small molecule alone.

Figure 8: PFPA-Zwitterion Copolymer Polymerization



The PFPA-zwitterionic copolymer was made under air-free conditions using a process called atom-transfer radical polymerization.

Source: "Biofouling resistant coatings and methods of making and using the same" US20200385506A1

The general process of attaching PFPAs to the surface of membranes is shown in Figure 9. Once a solution of PFPA derivative was prepared, a piece of membrane was submerged in the solution. While the membrane was still wet with the solution, it was placed under a UV lamp for enough time to activate the N_3 groups and bind the PFPAs to the surface. Rinsing the membrane removed any excess, unbound PFPA. Then, the membrane was prepared for testing.



Figure 9: Process of Modifying Membranes Using Photochemistry

Once the PFPA derivative is made, membranes can be modified in a single step.

By measuring the degree to which water spreads out on a surface, the researchers were able to evaluate the effect of the PFPA coating. If the inner angle between a water droplet and the surface is reduced, the surface is more hydrophilic. In general, the goal was to increase the hydrophilicity of surfaces. Figure 10 shows how the contact angle changes depending on the amount of the PFPA-copolymer that is applied to the surface. These modified surfaces were compared to the unmodified commercial membrane as well as to a membrane treated with UV light alone. UV irradiation alone does not cause a significant increase in hydrophilicity. Therefore, the improvement in hydrophilicity was due to the copolymer, not the UV treatment.

Figure 10: Copolymer Modification Makes Membranes More "Water Loving"



In general, adding more copolymer makes membranes more hydrophilic than untreated membranes and membranes exposed to UV light only. Images of the water droplets on the surface of unmodified and modified membranes are shown in Figure 11. The top image shows a more circular water droplet — that is, the angle between the surface and the edge of the water droplet is greater. The bottom image is "flatter": the angle between the surface and the top of the water droplet is much smaller as the water has a greater affinity for the hydrophilic membrane surface.

PFPA-modified Membranes Fouling Experiments

To show the efficacy of the surface coatings, modified and unmodified membranes were tested in a lab-scale, pressurized cross-flow apparatus. This type of setup is the most realistic simulation of a commercial setup.

Bovine Serum Albumin

As mentioned in the Introduction, there are two general types of fouling: one caused by the accumulation and/or growth of organic material on the surfaces of membranes, and the other by the accumulation of salt crystals on the surfaces of membranes as the solution becomes overly saturated with salt as the clean water passes through the membrane. Bovine serum albumin (BSA) is often used as a model foulant for membranes. Small amounts of BSA were included in the salty feed stream. As the experiment proceeded, some of the BSA accumulated on the surface of the membranes, resulting in a decrease in water flux through the membrane. Project results show that the membrane modification did not negatively impact the ability of the membrane to reject salt nor reduce significantly the water flux through the membrane. While some reduction in flux was observed for modified samples, it was more easily reversed with cleaning. Figure 11 shows two membranes after a fouling experiment. The unmodified membrane (top) is very yellow in color, indicative of extensive fouling. The modified membrane (bottom) shows very little visible fouling implying that adhesion and accumulation of BSA on the membrane surface was greatly reduced.



Figure 11: Modified Membranes That Are More Hydrophilic Are Less-Easily Fouled

Left: Contact angle images of unmodified (top) and PFPA-zwitterion copolymer modified membrane (bottom). The water droplet spreads out on the modified membrane surface because of the modification's affinity for water. Right: Corresponding images of the unmodified (top) and modified (bottom) RO membranes after a fouling experiment has been conducted. Turning to the PFPA-TANI modification, Figure 12 gives an example of fouling experiments using BSA. While in both cases a flux decline is observed, the flux decline was reduced by nearly 10 percent even within the first hour of fouling. With additional rinse steps, this trend of reduced irreversible fouling was also observed in longer-term studies.



Figure 12: Measuring Water-flux Decline Gives an Idea of Modification Efficacy

The membrane modified with PFPA-TANI had a lower decline in short-term flux than the unmodified polyethersulfone (PES) membrane.

Source: Lin et al., 2019

Mineral Scaling

Membrane scaling is a problem that occurs in all membrane processes where aqueous minerals are in the feed water. As pure water is generated in the permeate, the concentration at the interface of the feed and the membrane becomes highly concentrated and as the solutes reach their solubility limit, they precipitate out of solution onto the membrane. These crystals then act as seeds for further crystal growth on the membrane surfaces. Methods of scaling reduction include increasing how fast the water passes across a membrane, adding chemical antiscalants (usually surfactant formulations), and carefully monitoring the pH to avoid ideal saturation conditions. To test the anti-scaling properties of the modified membranes, the team developed a system for accelerated scaling.

In these experiments, the feed was comprised of the ions at concentrations indicated in Table 1. The membrane used was a DOW BW30XLE membrane pressurized at 150 pounds per square inch under a crossflow stream of 2.33 centimeters per second.

Constituent	mM*
Na+	30
Ca2+	6.73
Mg2+	5.97
K+	0.41
Cl-	30.41
SO42-	12.70

Table 1: Foulant Ions and Their Concentrations

*Millimolar

Unlike biofouling experiments, the normalized flux for modified and unmodified membranes appeared to be nearly identical for the control and modified membranes (Figure 13a-b). On the other hand, the turbidity of the feed stream remained lower for the modified membrane (Figure 13c-d). Additional experiments need to be performed to confirm whether this effect was indeed due to less reduced surface precipitation and thus lower suspended solids in the feed stream (unlikely due to controlled pH, temperature, and crossflow velocity), as opposed to some experimental variation. The expected reduction in rejection of total dissolved solids (TDS) and increase in retentate stream TDS was similar for the control membrane and the modified membranes (Figure 13c-d). The modified membrane showed lower TDS rejection over the course of the experiment and increased calcium ion concentration but showed a slower decrease in rejection compared to the modified membrane (Figure 13a-b). This could be due to a reduced rate of surface scaling, but the explanation for the lower overall rejection is unclear. Previous experiments showed that the modification had little to no effect on membrane rejection; in some cases, there was a small increase. Additional experiments are needed to confirm the source of these differences, which could be due to differences in interfacial forces at the membrane surfaces or variations in the original membrane coupons.

Unlike the analytical results shown in Figure 13, scanning electron microscope (SEM) images (Figure 14) show an obvious difference in the scaling layers between modified and unmodified membranes. While the modified membranes were completely covered in salt crystals, the individual nucleation sites on the modified membrane appeared to be spaced apart. These differences suggest that nucleation at the surface was slowed due to the membrane modification, thus crystal growth was limited. A technique that measures elemental composition called "energy-dispersive X-ray spectroscopy" (EDS) confirmed that the overall concentration of salts was lower on the surface of the modified versus the unmodified membranes.

These results are promising, but while the mechanism to prevent scaling may be similar to that of fouling, more hydrophilic surfaces keep salts from precipitating onto the membrane surfaces. However, much work needs to be done regarding this application.



Figure 13: Simulated Mineral Scale on Brackish Water Desalination Membranes

(a-b) As more water passes through the membrane, the rate of water passing through the membrane declines. (c-d) Calcium ion removal is slightly higher for the modified membrane vs. the unmodified membrane. (e-f) As the experiment progresses and clean water is recovered, concentrations of solutes in the feed solution increase.



Figure 14: Images of Mineral Scale on Membranes

SEM images of control (top left) and modified (bottom left) membranes showing the crystallinescale layer. EDS, elemental analysis for control (top right) and modified (bottom right) membranes, showing higher salt content on the surface of the unmodified membrane. Pt peaks are due to Pt sputtering performed to obtain the SEM images.

Bacterial Adhesion and Growth

Finally, the team tested the ability of PFPA-TANI modified membranes to resist bacterial adhesion and growth. Bacteria that is free-floating in water when allowed to adhere to a surface will create what is called a biofilm. Biofilms then grow and act as a haven for other bacteria, thus producing a colony, which is difficult to remove and can create permanent damage to the membranes. PES membranes modified with the PFPA-TANI monomer and without modification were cultured with *E. coli*. Figure 15 shows membrane surfaces where the green stain indicates the presence of live *E. coli* cells, while the red stain indicates dead *E. coli*. The PFPA-TANI modified membranes show little bacterial present either live or dead when compared to the unmodified membranes. The purpose of the live/dead stain was to show that the surface was not "killing" bacteria on the surface, but simply preventing their adhesion in the first place.



Figure 15: Bacteria Cultured on PFPA-TANI Modified PES Membranes

Accumulation of bacteria was greatly reduced on PFPA-TANI-modified PES membranes.

Roll-to-Roll Prototype Development

As a proof-of-concept, a miniature roll-to-roll coating system was developed in the lab. This apparatus created a continuous process to include the three steps of modifying a membrane: saturating in the PFPA solution, UV-initiation of surface modification, and rinsing of modified material of non-bound modifier. Figure 16a shows a flat sheet being submerged into a PFPA solution and then being exposed to UV light. The project's actual prototype is shown in Figure 16b-c in which a roll of polyethylene was unwound and introduced to a PFPA solution. The film

was then passed under a UV-light source before being fed into a water bath that, assisted by agitation, cleaned any excess chemical from the film's surface. The modified sheet was then rolled onto a second spool.



Figure 16: Small Proof-of-Concept Roll-to-Roll Modification of Plastic Film with PFPA Derivative

(a) Concept image of the roll-to-roll process. (b) Bottom to top: actual lab-scale roll-to-roll setup with initial roll, solution bath, UV light source, sonication (cleaning) bath, and final roll. (b) is an image of (c) from left to right.

T-FLO Membranes for Tailored Selectivity

Optimization of Mechanical Properties

The amount of energy consumed by a membrane process has a lot to do with the mechanical properties of the material against which water is being pressurized. If a material is soft, with a lot of holes in it, it will take less energy to force water through it. If a material is thick and dense, more energy is required to force water through it. When developing a way to make asymmetric membranes from difficult-to-process materials, the research team wanted to reduce the negative impacts of using these materials, including reduced water flux and mechanical fragility. At the same time, support layers needed to be robust enough to resist being crushed (the pores collapsing) under the high pressure required for operation.

The chemistry of the T-FLO membranes' epoxy support layers is highly tunable. By using different types of polyethylene glycols (PEG) porogen, the team was able to tune the kinetics of epoxy polymerization, which directly affected the pore structure of the resulting epoxy

supporting membrane. Membranes with short-chain PEG porogen as a larger proportion of end-groups per unit mass result in more porous membrane. In contrast, using primarily longchained PEGs leads to a denser membrane structure. The range of pore density that could be achieved using this technique is demonstrated in Figure 17a, where porous membranes appear more opaque and membranes with smaller pores are increasingly transparent. This was useful because the same support layer chemistry can result in different membrane structures. Active layers or applications that require membranes to withstand higher pressures may benefit from a denser, less-compactable support. On the other hand, higher flux membranes may require a looser support layer structure that provides less resistances. Figure 17b shows the flux versus time for an asymmetric RO membrane with very large pores in red, where the membrane compacts; the flux decreases very rapidly. On the other hand, the black line is the trace for a membrane with optimized porogen chemistry, in which the flux is extremely stable. This ability to optimize support structures for unique active layers may be useful in minimizing the resistance a support layer creates, thus saving energy, while providing enough support to resist severe compaction.



Figure 17: Mechanical Tuning of Epoxy Membranes

(a) Circular cutouts of epoxy-support membranes made with increasing PEG 400 to PEG 200 porogen. (b) Flow rate vs. time for complete thin-film composite membranes with a highly porous support layer (red) and an optimized support layer (black). (c) Water flux through bare support membranes as a function of PEG 200:PEG 400 ratio.

Selective Desalination Using Polybenzimidazole Blends and Derivatives

Using T-FLO as a platform, the research team intensively studied the nature of polybenzimidazole, its derivatives, and blends while trying to better understand how to tune its selectivity based on acid-base and dispersion forces at the feed-membrane interface. Previous reports by the researchers shared data on the Cl tolerance of the polybenzimidazole (PBI)-polystyrene sulfonic acid (PSSA) composite active layer as well as its rejection of brackish water containing concentrated NaCl.

Figure 18 includes three polymers: celazole-PBI, PSSA, and sulfonated PBI (SPBI-48) and includes the effects of water pH on their surface charge. Fully protonated and deprotonated states are shown. PBI has either a positive surface charge or a neutral surface charge. PSSA shows either a neutral charge or a negative charge, and SPBI-48 can have either positive, neutral, or negative surface charge. Apart from this, dispersion and electron donating/ accepting components of the membrane surface energy were calculated using the extended Young-Dupree equation and contact angle measurements using three probe liquids: diiodomethane, deionized water, and ethylene glycol. A sampling of these data is given in Table 1. The research team's continuing work is to make correlations between rejection, charge, and surface energy components. The team has performed dead-end cell tests to compare rejection values of 35,000 parts per million NaCl based on the pH of the feed. Combined with pH titration and ζ (Zeta potential) measurements, the team hopes to gain a robust understanding of these effects on ion and small molecule transport through thin films. The end goal for these experiments is to develop a methodology for tuning the selectivity of these highly chemically tolerant materials for desalination and trace pollutant removal.





Chemical structures of polymers used: PBI (left), PSSA (center) and SPBI-48 (right).

Performance of T-FLO Membranes

The project aimed to reduce the energy required to purify inland, brackish groundwater and other contaminated sources. One way of reducing energy is to reduce membrane fouling by biofilm forming microorganisms as well as mineral scaling. Both processes cause reduced permeate production with applied pressure, increased need for backwashing (a process that uses energy but does not produce any additional clean water), and ultimately, more frequent replacement of membrane modules. One of the ways to reduce membrane fouling is by attaching small molecules or polymers to the surface of commercial membranes using scalable photochemistry then evaluating their effect on recoverable flux and bacterial adhesion. Another angle is to explore the use of novel materials, their processing, and use in fabrication of new types of membranes. Paired with review of the state-of-the-art technologies used for inland brackish water purification, it is possible to assess the economic viability of implementing various solutions.

Surface energy components determined using contact angle measurements and the extended Young-Dupree equation are summarized in Figure 19. PBI shows the lowest interfacial surface tension, largely due to the relatively low contribution of the Lifshitz-van der Waals component (γ^{LW}). This can be explained on a chemical basis by the sulfonate groups, which are present in their sulfonated and blended forms. Sulfonate groups provide the largest electron accepting character, and PBI is a basic polymer, suggesting that this may be due to the polymer being, on average, more electron deficient regardless of its acidic or basic character. SPBI, on the other hand, has the highest number of large atoms per unit mass. Therefore, as a system, SPBI has greater electron polarizability giving rise to higher interactions in Van der Waals free energies, γ^{LW} and γ^{-} .



Figure 19: Values Summarizing Surface Chemistry of Membranes

Each of the materials in this figure has different surface properties that correlate with how atoms in the polymer chains are linked together.

As a part of this basic science project, the research team presents more research on the water chemistry aspects of this study — in particular, the effects of pH and the capacity for salt rejection.

Rejection of charged molecules by a membrane is dependent on a combination of several factors, a crucial one being surface charge. Because of the acidic, basic, or amphiphilic nature of the polymers and polymer blends presented previously, the surface charge (positive, negative, or zero) is largely dependent on pH. Two methods of measuring the pH dependence of surface charge are ζ -potential measurements and contact angle titration. The isoelectronic point of each membrane, the ability to tune the surface charge using only these three polymers in their native forms, or as blends, would be observed. Furthermore, by adjusting the ratio of the blends, the isoelectronic point can be adjusted between the ranges of the native forms.

With the same membranes, several dead-end cell tests of NaCl rejection were performed to investigate correlations between rejection and pH of feed water, the ζ-potential traces and other variables. Significant rejection of monovalent-salts by PBI is not widely reported, although this has been achieved with cross-linked formulations. Therefore, the data presented here for NaCl is primarily for the study of charge on the membrane surfaces, not for optimizing rejection of NaCl. Figure 20 gives the results from six dead-end tests of the rejection of seawater concentrations of NaCl. At first glance, the rejection trends of NaCl by PBI and PBI/PSSA appear to be opposite. This tracks with chemical intuition, which is that PBI cannot be deprotonated, so it would have its highest rejection at low pH, where it can be positively charged. On the other hand, PBI/PSSA, which can be both protonated and deprotonated, shows higher rejection with the PSSA when it is deprotonated, but equivalent rejection to PBI at lower pH. Less obvious is the effect of either ζ -potential or surface tension components on this trend and the Isoelectric Point and surface potentials across the pH scale are similar. pH drops across the samples were comparable enough between the two samples as to not be the likely causes of the differences. Although speculative, there may be a correlation between y^{LW} and rejection at higher pH, perhaps due to greater electron density and cloud-polarizability for the OH-containing feed-water and successive effects on Na⁺ ion passage. A significant amount of work remains to be done to fully understand the tunability of these membrane systems for RO applications.



Figure 20: NaCl Removal from Water of Varying Chemistries

This is a sample dataset demonstrating how different water chemistries affect how well the membranes remove salt from water.

In conclusion, multivariate analyses will likely be needed as the true correlations between physical, chemical, and solute/solvent interactions are likely more accurately represented in higher-dimensional space. In the meantime, normalization of rejection by polymer crystallinity, active layer thickness, and other spectral properties can be carried out to see if there is a reinforcement of this preliminary trend. The remainder of the salt-rejection data, that is, that from SPBI/PSSA and SPBI, may also shed more light on trends. These experiments are in progress.

Graphene Oxide T-FLO Membranes

In addition to the creation of new membranes for RO, the research team made and evaluated membranes using materials, such as graphene oxide (GO). Although most membranes created claiming to use the unique properties of carbon materials like GO receive a lot of attention, many of their designs are not practical for large-scale membrane manufacture nor do they have the robustness needed for real-world membranes. Using a method of membrane fabrication discussed earlier for polymeric active layers, the research team attempted to overcome these challenges.

GO suspended in water at concentrations of 2.5 milligrams per gram (mg/g), 5 mg/g, 7.5 mg/g, and 10 mg/g were cast onto glass substrates forming dry films 32 nanometer (nm) to 131 nm thick (measured using step profilometry and/or scanning electron microscopy). An epoxy-resin solution containing bisphenol A diglycidyl ether, bisphenol A propoxylate diglycidyl ether, piperazine, and 1-(2-aminoethyl) piperazine dissolved in PEG (molecular weight 400), which acts as a porogen, was then cast onto nonwoven glass fiber placed atop GO films. Following this basic method for T-FLO, epoxide groups were reacted with functional groups on the graphene oxide sheets, fixing them in place upon resin cure before delaminating upon submersion in a water solvent exchange bath. These films were denoted "lifted" GO (LGO) and were compared to "conventional" GO (CGO) films made by filtering GO solutions through a pre-made polymer support pad.

X-ray diffraction patterns were generated as X-rays from a monochromatic beam constructively or destructively interfered after they interacted with a crystalline material at varying angles. In the case of graphene and graphene oxide, the concern was with the spacing between monolayer thick sheets of carbon atoms, which can be calculated by the angle of maximum constructive interference. The large number of oxygen functionalities on the surface of GO sheets caused the material to swell when wet thus increasing the spaces between the sheets. Because the heat treatment processes led to some thermal reduction (loss of oxygen functionalities) of the GO, LGO had an overall smaller interlayer spacing compared to CGO as observed by the difference of peak positions in their X-ray diffraction patterns.

To find out what type of water contaminants might be removed using this type of film, rejection of different dyes as well as salts covering a range of hydrated radii (a measurement of how large the particles are in water when surrounded by a layer of water molecules) was tested in a pressurized dead-end cell. As can be seen in Figure 21a, high rejection (greater than 98 percent), was maintained for solutes with hydrated radii of 4.87 angstroms or larger, while rejection diminished for solutes with smaller radii, including salts. Figure 21b shows the relationship between film thickness, percent rejection of dyes and permeability of solvent through the films. Membrane permeability is a function of film thickness, while rejection is a function of the material. From these experiments we can infer that membrane perm-selectivity is dictated by the dense GO layers.





(a) Percentage of dye removed by a membrane vs. the hydrodynamic radius of a dye as a function of the hydrodynamic radius of the dye for T-FLO-GO membranes and conventional GO membranes. (b) Flux and rejection as a function of GO layer thickness.

Graphene

Single layered graphite, known as graphene, is popular in materials research for energy storage and composite applications because of its high conductivity and large surface area. It is of interest for water purification because of the way that water can rapidly permeate through a network of graphene sheets. GO, commonly used as a precursor to reduced graphene oxide, which has similar properties to graphene, can be made in large batches from graphite through an exfoliation process. Unlike graphene, GO has many oxygen functionalities that make the material more hydrophilic and offer handles for chemical modification. Using the T-FLO method, epoxy resin was reacted with the oxygen moieties on the GO and then converted to a porous membrane support for the GO layer.

Figure 22a shows the top surface of an LGO film using scanning electron microscopy. This image shows a smooth, continuous active layer with no large pinholes. The thickness of the active layer can be controlled by the concentration of GO in solution. Figure 22b shows a cross-section of an LGO film indicating an active layer smaller than 100 nm. The porous support voids appear to be greater than or equal to 100 nm. Atomic force microscopy was used to study the topography of the LGO films. The surfaces were found to be quite smooth. X-ray photoelectron spectroscopy was used to characterize the surface of LGO membranes. The deconvolution of the Cl's peak approximates the different C-O bonds found on the surface of the LGO film, which show only minimal differences from the GO sample from which the membrane sample was made. This indicates that the characterization of GO before film

formation was an accurate reflection, with only minor functionality changes, of the GO that made up the active layer.

In addition to work with GO, the research team continues to work on RO membranes using similar liftoff techniques but using polymer thin films that can be cleaned with Cl and thus reduce the high operational energy requirements caused by membrane fouling. With regard to work with modifications of commercial membranes, the team is in the process of trouble-shooting standard procedures for membrane scaling experiments using a crossflow system.



Figure 22: T-FLO Membrane with a GO Active Layer

(a) Surface of T-FLO GO membrane. (b) Cross-sectional image of a T-FLO GO membrane.

Gas Separation Membranes

To show that high quality dense membranes can be made using T-FLO, gas permeation experiments were carried out. The composite membranes chosen contained a combination of the conjugated polymer polyaniline and graphite oxide. Gas permeability tests using N and carbon dioxide (CO₂) indicated that the membranes were fully dense with no pinholes (Figure 23).



Figure 23: Gas Separation Membranes Made Using T-FLO

(a) Gives the permeability of N and CO₂ and N gases for polyaniline (PANi)/GO membranes. Because the permeability is so much higher for N₂ than CO₂, it can be said to efficiently separate the two gases. (b) A micro-scale image of a T-FLO gas separation membrane.

Source: McVerry et al., 2019

CHAPTER 4: Technology/Knowledge/Market Transfer Activities

Technology Transfer

Some of the work performed under this research builds on patented material previously developed by the authors. These include the PFPA-copolymer technology (Biofouling Resistant Coatings and Methods of Making and Using the Same, U.S. patent 20200385506A1) and the T-FLO technique (Asymmetric Composite Membranes and Uses Thereof, U.S. patent 2020026 1855A1). Beachhead markets of these patented works are hospitals and other healthcare providers where patients require frequent catheterization. The efficacy of the coating for infection reduction needs to be observed in large, catheterized populations, but currently, lubricity alone makes coated catheters potentially marketable. In general, silicone is a high-friction material. Therefore, making smoother silicone has many wet and dry applications in medical devices and consumables. Additionally, functionalized polyethylene has applications in battery technology, to improve the "wettability" of battery separators to enable safer solvents to be used in battery electrolytes. Although tangential to the original work, these applications could be useful for improving the safety of on-site "battery farms" used in the electrification of buildings and communities.

A more recent patent acknowledging the CEC and U.S. CERC-WET funding of this work includes a patent entitled "Highly Permeable Graphene Oxide/Polyaniline Thin Film Membranes for CO₂ Separations from Flue Gas" (UC 2019-861). With CERC-WET, University of California, Los Angeles partner Prof. Gaurav Sant worked on the use of CO₂ in cement production and found the T-FLO technique could be used to make membranes that can separate CO₂ from other waste gases. Separation of this greenhouse gas from mixtures could prove to be very helpful as industries work on reducing CO₂ emissions.

Market Outlook

Long-term target markets for the PFPA technologies are membrane manufacturers who could integrate the roll-to-roll process into their spiral-wound membrane module fabrication. According to a study performed by Grandview Research, the compound average growth rate for the spiral wound membrane market worldwide is 10.6 percent. In addition to being used for water and wastewater treatment, membranes are used in the food and beverage processing industries, which represent the third largest manufacturing industry in California and the second largest membrane market globally, the largest being wastewater treatment. According to Jafara et al., (2020), replacement of modules damaged by fouling and the increase in energy use required when using fouled membranes comprise between 11 percent and 24 percent of a membrane facility's operating expenditure.

CHAPTER 5: Conclusions

The Role of Policy in Membrane Technology Advancement

Incentivization programs, such as those put forward in Senate Bill 1477 to make buildings carbon-neutral, could also increase the likelihood of adoption of low-fouling membranes for water treatment facilities. Membrane modification does not interfere with current infrastructure and can continue to be applied to novel membrane modules or in membrane modules with updated pumping infrastructure. Additional policy incentivizing low-energy consumption for water purification and distribution could benefit membrane technology adoption.

Targets for urban centers to become independent from imported water supplies could promote water recycling efforts. Reducing policies that limit the use of recycled water to very particular applications is essential to achieving water independence and the realization of the full potential of membrane technologies. Campaigns that focus on educating the public about the efficacy of membrane separation technologies can help reduce the negative sentiment that many have toward using recycled wastewater. Ensuring that the public knows a particular water supply is safe is very important for the realization of technological benefits of any kind.

A policy to encourage the use of more energy efficient membrane technologies can be one that disincentivizes waste production at membrane sites. Given that spiral wound modules are not recyclable, state policies regarding the amount of waste generated by plants are one way to incentivize technology adaptation. Higher priced modules that last longer may therefore reduce operating expenses and make use of renewable energy in RO more attractive.

Information for the Design of Energy-Efficient Membrane Treatment Facilities

While the details that go into planning a new water treatment facility are not top-of-mind for many Californians, the authors' book entitled *Sustainable Desalination and Reuse* provides an accessible overview for policy makers, city planners, and project oversight committees to understand the possibilities and limitations of membrane technologies and to provide context for where the technology is heading and what future/improved technologies may provide.

CHAPTER 6: Benefits to Ratepayers

California has strict policies regarding desalination and reuse. This research contributes to improving the energy efficiency of technologies that will make California's cities, and the state as a whole, more water independent. Prior to the building of water treatment infrastructure, its energy efficiency needs to be understood in whole.

A potential benefit to all ratepayers is improved access to sustainable sources of fresh water through the treatment of brackish water and wastewater.

Reducing the impact of fouling may reduce the operating expense of a desalination facility and extend the life of membrane modules.

GLOSSARY AND LIST OF ACRONYMS

Term	Definition
ACS	American Chemical Society
AWWA	American Water Works Association
BSA	bovine serum albumin: a model organic foulant
CA ²⁺	calcium cation
CEC	California Energy Commission
CERC-WET	Clean Energy Research Center for Water-Energy Technologies
CGO	conventional graphene oxide
Cl	chlorine
Cl-	chlorine ion
CO ₂	carbon dioxide
CO ₃ ²⁻	carbonate ion
COD	chemical oxygen demand
EDS	energy-dispersive X-ray spectroscopy: a technique that measures elemental composition
EPIC	Electric Program Investment Charge
GO	graphene oxide: single sheets of graphite with lots of oxygen groups
K+	potassium ion
LGO	lifted graphene oxide
mg/g	milligrams per gram
mM	millimolar
mV	viscosity average molar mass
N	nitrogen
N ₃	azide
Na ⁺	sodium
NaCl	sodium chloride
NF	nanofiltration
NH ₂	amine group
nm	nanometer
NO ₃ ²⁻	beryllium nitrate
OSN	organic solvent nanofiltration
PANi	polyaniline

Term	Definition
PBI	polybenzimidazole: a type of chemically resistant plastic
PEG	polyethylene glycol
PES	polyethersulfone: a type of plastic used to make nanofiltration membranes
PFPA	perfluorophenylazide: the chemical group that reacts photochemically with surfaces and anchors chemical modifiers to surfaces
PSSA	polystyrene sulfonic acid
Pt	platinum
rGO	reduced graphene oxide
RO	reverse osmosis
S	sulfur
SEM	scanning electron microscope
SO4 ²⁻	sulfate
SPBI	A type of PBI that has sulfonate groups attached that give the surface a negative charge in alkaline water
TANI	tetraaniline: a short chain of four aniline molecules
TDS	total dissolved solids
TFC	thin-film composite
T-FLO	thin-film liftoff: a technique the research team developed to make asymmetric membranes in which a thin film is lifted off of a substrate by a cured polymer support
UF	ultrafiltration
UV	ultraviolet
Y ^{LW}	Lifshitz-van der Waals component
ζ	Zeta

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ENERGY RESEARCH AND DEVELOPMENT DIVISION

Appendix A: Abstracts for Papers on Asymmetric Membranes Made Using Thin-Film Liftoff

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APPENDIX A: Abstracts for Papers on Asymmetric Membranes Made Using Thin-Film Liftoff

Next-Generation Asymmetric Membranes Using Thin-Film Liftoff

For the past 30 years, thin-film membrane composites have been the state-of-the-art technology for reverse osmosis (RO), nanofiltration (NF), ultrafiltration, and gas separation. However, traditional membrane casting techniques, such as phase inversion and interfacial polymerization, limit the types of material that are used for the membrane separation layer. Here, we describe a novel thin-film liftoff (T-FLO) technique that enables the fabrication of thin-film composite membranes with new materials for desalination, organic solvent (NF), and gas separation. The active layer is cast separately from the porous support layer, allowing for the tuning of the thickness and chemistry of the active layer. A fiber-reinforced, epoxy-based resin is then cured on top of the active layer to form a covalently bound support layer. Upon submersion in water, the cured membrane lifts off from the substrate to produce a robust, freestanding, asymmetric membrane composite. We demonstrate the fabrication of three novel T-FLO membranes for chlorine-tolerant rRO, organic solvent NF, and gas separation. The isolable nature of support and active-layer formation paves the way for the discovery of the transport and selectivity properties of new polymeric materials. This work introduces the foundation for T-FLO membranes and enables exciting new materials to be implemented as the active layers of thin-film membranes, including high-performance polymers, twodimensional materials, and metal-organic frameworks.

McVerry, B., M. Anderson, N. He, H. Kweon, C. Ji, S. Xue, E. Rao, C. Lee, C.W. Lin, D. Chen, D. Jun, F. Sant, and R.B. Kaner. (2019). "Next-Generation Asymmetric Membranes Using Thin-Film Liftoff." *Nano Letters*, 19(8), 5036–5043. Available at <u>https://doi.org/ 10.1021/acs.nanolett.9b01289</u>.

Highly Permeable Polyaniline–Graphene Oxide Nanocomposite Membranes for CO₂ Separations

Carbon dioxide (CO₂) capture from fossil-fuel-based power plants requires scalable membranes with high CO₂ permeability and reasonable CO₂/N₂ selectivity. Conventional membranes based on PANi feature a CO₂ permeability of 1 Barrer or less, which is unviable for industrial applications such as separating the massive scale of CO₂ emissions produced by power plants. Here, we report nanocomposites comprised of the conjugated polymer polyaniline with graphene oxide at different oxidation levels that are blended and drop-cast to form freestanding membranes for gas separations. The added graphene oxide is shown to effectively enhance the gas permeability. These hybrid membranes are characterized by Fourier-transform infrared spectroscopy to indicate clearly the presence of well-dispersed GO in the polyaniline matrix; vertical scanning interferometry and field emission scanning electron microscopy to illustrate the film homogeneity, morphology, and thickness; and thermogravimetric analysis to assess

thermal stability. The outcomes highlight composited membranes that are readily scalable, tolerant to slightly elevated temperatures (up to 338°F [170°C]), and that feature CO₂ permeabilities >700 Barrers and reasonable CO₂/N₂ selectivities. By applying a doping/ dedoping/redoping process using hydrochloric acid (HCl) and ammonium hydroxide (NH₄OH), the membrane selectivities can be considerably enhanced. This work thus reports the first synthesis of PANi-based nanocomposite membranes whose permeability begins to approach the upper bound indicated on a Robeson plot.

Kweon, H., C.W. Lin, M.M. Faruque Hasan, R. Kaner, and G.N. Sant. (2019). "Highly Permeable Polyaniline–Graphene Oxide Nanocomposite Membranes for CO₂ Separations." ACS Applied Polymer Materials, 1(12), 3233–3241. Available at <u>https:// doi.org/10.1021/acsapm.9b00426</u>.

Nanostructured Graphene Oxide Composite Membranes with Ultrapermeability and Mechanical Robustness

Graphene oxide (GO) membranes have great potential for separation applications due to their low-friction water permeation combined with unique molecular sieving ability. However, the practical use of deposited GO membranes is limited by the inferior mechanical robustness of the membrane composite structure derived from conventional deposition methods. Here, we report a nanostructured GO membrane that possesses great permeability and mechanical robustness. This composite membrane consists of an ultrathin selective GO nanofilm (as low as 32 nanometers (nm) thick) and a postsynthesized macroporous support layer that exhibits excellent stability in water and under practical permeability testing. By utilizing thin-film liftoff (T-FLO) to fabricate membranes with precise optimizations in both selective and support layers, unprecedented water permeability ($47 L \cdot m^{-2} \cdot hr^{-1} \cdot bar^{-1}$) and high retention (>98 percent of solutes with hydrated radii larger than 4.9 Å) were obtained.

Xue, S., C. Ji, M.D. Kowal, J.C. Molas, C.W. Lin, B.T. Mcverry, C.L. Turner, W.H. Mak, M. Anderson, M. Muni, E.M.V. Hoek, Z.L. Xu, and R.B. Kaner. (2020). "Nanostructured Graphene Oxide Composite Membranes with Ultra-permeability and Mechanical Robustness." *Nano Letters*. Available at <u>https://doi.org/10.1021/acs.nanolett.9b03780</u>.

Ultrapermeable Organic Solvent Nanofiltration Membranes with Precisely Tailored Support Layers Fabricated Using Thin-Film Liftoff

Thin-film composite (TFC) membranes are favored for precise molecular sieving in liquid-phase separations; they possess high permeability due to the minimal thickness of the active layer and the high porosity of the support layer. However, current TFC membrane fabrication techniques are limited by the available materials for the selective layer and do not demonstrate the level of structural control needed to substantially advance organic solvent nanofiltration (OSN) membrane technology. In this work, we employ the newly developed thin-film liftoff (T-FLO) technique to fabricate polybenzimidazole (PBI) TFC membranes with porous support layers uniquely tailored to OSN. The drop-cast dense PBI selective layers endow the membranes with an almost complete rejection of common small dye molecules. The polymeric support layer is

optimized by a combinatorial approach using four different monomers that alter the crosslinking density and polymer chain flexibility of the final composite. These two properties substantially affect the porogen holding capacity of the reticular polymer network, leading to the formation of different macropore structures. With a 150 nm thick PBI selective layer and fine-tuning of the support layer, the resulting membrane achieves stable and superior permeance of 14.0, 11.7, 16.4, 11.4, 17.1, and 19.7 L m⁻² h⁻¹ bar⁻¹ for water, ethanol, methanol, isopropanol, tetrahydrofuran, and acetonitrile, respectively.

Ji, C., S. Xue, C.W. Lin, W.H. Mak, B.T. McVerry, C.L. Turner, M. Anderson, J.C. Molas, Z. Xu, and R.B. Kaner. (2020). "Ultrapermeable Organic Solvent Nanofiltration Membranes with Precisely Tailored Support Layers Fabricated Using Thin-Film Liftoff." ACS Applied Materials and Interfaces, 12(27), 30796–30804. Available at <u>https://doi.org/10.1021/</u> acsami.0c06639.





ENERGY RESEARCH AND DEVELOPMENT DIVISION

Appendix B: Abstracts for Papers on Membranes Modified Using PFPA Photochemistry

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APPENDIX B: Abstracts for Papers on Membranes Modified Using PFPA Photochemistry

Direct Grafting of Tetraaniline via Perfluorophenylazide Photochemistry to Create Antifouling, Low Bio-adhesion Surfaces

Conjugated polyaniline has shown anticorrosive, hydrophilic, antibacterial, pH-responsive, and pseudocapacitive properties making it of interest in many fields. However, in situ grafting of polyaniline without harsh chemical treatments is challenging. In this study, we report a simple, fast, and nondestructive surface modification method for grafting tetraaniline (TANI), the smallest conjugated repeat unit of polyaniline, onto several materials via perfluorophenylazide (PFPA) photochemistry. The new materials are characterized by nuclear magnetic resonance and electrospray ionization mass spectroscopy. TANI is shown to be covalently bonded to important carbon materials including graphite, carbon nanotubes, and reduced graphene oxide (rGO), as confirmed by transmission electron microscopy. Furthermore, large area modifications on polyethylene terephthalate films through dip-coating or spray-coating demonstrate the potential applicability in biomedical applications where high transparency, patternability, and low bio-adhesion are needed. Another important application is preventing biofouling in membranes for water purification. Here we report the first oligoaniline grafted water filtration membranes by modifying commercially available polyethersulfone (PES) ultrafiltration (UF) membranes. The modified membranes are hydrophilic as demonstrated by captive bubble experiments and exhibit extraordinarily low bovine serum albumin (BSA) and Escherichia coli adhesions. Superior membrane performance in terms of flux, BSA rejection and flux recovery after biofouling are demonstrated using a cross-flow system and dead-end cells, showing excellent fouling resistance produced by the *in situ* modification.

Lin, C.W., S. Aguilar, E. Rao, W.H. Mak, X. Huang, N. He, D. Chen, D. Jun, P.A. Curson, B.T. McVerry, E.M.V. Hoek, S.C. Huang, and R.B. Kaner. (2019). "Direct grafting of tetraaniline via perfluorophenylazide photochemistry to create antifouling, low bioadhesion surfaces." *Chemical Science*, 16(10), 4445-4457. Available at <u>https://doi.org/ 10.1039/c8sc04832k.</u>





ENERGY RESEARCH AND DEVELOPMENT DIVISION

Appendix C: Abstracts from Papers on Membrane Processes and Theory

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APPENDIX C: Abstracts from Papers on Membrane Processes and Theory

Performance, Energy and Cost of Produced Water Treatment by Chemical Coagulation and Electrochemical Coagulation

The separation performance, energy demand, and operating costs of electro-coagulation (EC) are compared to conventional chemical coagulation for oil–water separation using a simulated oil- and gas-produced water matrix. An iron-based chemical coagulant and sacrificial iron electrodes are evaluated. Effluent turbidity, chemical oxygen demand (COD), total organic carbon, and oil and grease (O&G) removal were determined for various coagulant concentrations and reaction times and current densities. Chemical coagulation produced superior turbidity removal when scaled by the total iron dose. At lower iron doses (<500 mg/L), chemical coagulation yielded better COD, turbidity, and O&G removal. However, chemical coagulation was unable to effectively remove contaminants to meet the offshore discharge limit of 29 parts per million O&G. At higher iron doses, EC was more effective at removing COD and O&G. The energy consumption of EC was found to be much higher even when factoring in the energy of production, transporting, and mixing of chemical coagulants, but the overall cost of EC was approximately half the cost of chemical coagulation, and more effective at O&G removal.

 Khor, C.M., J. Wang, M. Li, B.A. Oettel, R.B. Kaner, D. Jassby, and E.M.V. Hoek. (2020).
 "Performance, Energy and Cost of Produced Water Treatment by Chemical Coagulation and Electrochemical Coagulation." *Water*, 12(12), 1–14. Available at <u>https://doi.org/10.3390/w12123426</u>.

How permeable could a reverse osmosis membrane be if it was specifically developed for uncharged organic solute rejection?

Here, we present both experimental data and modeling results of the removal of four different polar organic solutes by six different commercial nanofiltration (NF) and reverse osmosis (RO) membranes in a natural groundwater matrix. These results are significant for two reasons. First, three of the polar organic solutes are contaminants commonly found in both drinking water aquifers and municipal wastewaters and, hence, are particularly relevant to the protection of public health in drinking water production and potable reuse applications. Second, our membrane transport model can be used (1) to understand the fundamental mechanism governing uncharged, polar organic solute rejection and (2) to make forward predictions about how one might alter NF/RO membrane chemistry and structure to achieve a desired level of rejection. Perhaps a disappointing conclusion is that, for uncharged, polar organic solutes, the only obvious means of improving rejection is to reduce pore size, increase barrier layer thickness, and/or decrease barrier layer porosity, all of which reduce water permeability and energy efficiency. However disappointing this conclusion may be, we believe the fundamental insights

that can be derived from this work are significant and important for the drinking water and water reuse scientific communities.

Wang, J., Y. Mo, B.T. McVerry, S. Mahendra, R.B. Kaner, and E.M.V Hoek. (2020). "How permeable could a reverse osmosis membrane be if it was specifically developed for uncharged organic solute rejection?" *AWWA Water Science*, 2(5), e1189, 1–14. Available at <u>https://doi.org/10.1002/aws2.1189</u>.