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GENERAL SUBMISSIONS
BIOMIMETIC MEMBRANES

1 **Biomimetic and Bioinspired Membranes: Opportunities, Challenges and New Directions**

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2 **Functional DNA As Versatile Building Blocks for Biomimicking Membranes.**

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Mangrove Membranes.

Mariusz Grzelakowski
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Mangrove Membranes

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Porins based membranes have been considered a promising filtration technology and have been intensively studied over the last few years[1]. Most common approach is to embed aquaporin, using lipid or block copolymer (BCP) vesicles, into membrane forming polymers on the porous substrates[2]. This approach has shown its limitations on number of occasions. The commercial membranes shown up to date failed to utilize selectivity and permeability of aquaporin or other porins in the separation layer. We have chosen an alternative approach to formation of active layer, where block copolymer vesicles serve as a vehicle for protein delivery and a coting material at the same time. Cross-linked block copolymer vesicles were successfully used to form separation layers. Membranes built this way were characterized by significantly increased water flux if polymer vesicles were reconstituted with aquaporins.

Here we will discuss the improvements to the original proof of concept[3], novel filtration membranes and scale up activities for production of membranes utilizing the functions of membrane proteins.

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Aquaporin-Based Biomimetic Reverse Osmosis Membranes: Stability and Long Term Performance.

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This study investigated the stability of the aquaporin-based biomimetic (ABM) membrane and its long-term reverse osmosis (RO) performance. A series of experiments showed that the ABM membranes exhibited good chemical stability after soaking in three commonly used chemical cleaning agents, namely ethylenediamine tetraacetic acid (EDTA), sodium hydroxide (NaOH) and citric acid, respectively. In addition, it was

found that both water permeability (flux per unit applied pressure) and solute rejection of ABM membranes are sensitive to the temperature and applied pressure. In the long-term RO performance evaluation, a real RO feed water from water reclamation process was used as feed; this is the first reported application of real RO feed water to ABM membranes. The membranes were periodically cleaned and the recovery of water permeability of the ABM membranes was found to be greater than 90%. The quality of the water permeate exceeded the World Health Organisation standard for drinking water. Compared with a commercial RO membrane, the ABM membrane only needed half of the applied pressure to achieve the same water flux, suggesting the advantage and potential of ABM membranes to reduce energy consumption in practical applications.

3 **Salt-Excluding Artificial Water Channels in Lipidic Systems.**

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Synthesis of High-Performance Biologically-Inspired Nanofiltration Membranes for Water Treatment.

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Aquaporins are membrane protein water channels present in cells, and they restrict the passage of contaminants including bacteria, viruses, minerals, proteins, DNA, dissolved gases, salts, detergents, and even protons without preventing the passage of water. Small molecules such as urea and boric acid, the removal of which is inefficient by conventional membranes are also rejected. Biomimetic membranes, an innovation in water filtration technology attempts to replicate a natural process occurring at the cell level; specifically, the highly-selective and efficient transport of different molecules across a cell membrane. Therefore, aquaporins have received worldwide attention because of their potential to form biomimetic membranes with high flux and selectivity for water reuse and desalination. However, challenges involved in the incorporation of aquaporin proteins in membranes limit their applicability. One of them is to attach aquaporins to the membranes without chemically altering or damaging the aquaporins during the binding to the membrane. The second challenge is to design and prepare an assembly that allows biomimetic membranes with aquaporins to sustain hydraulic water pressure gradients without losing their integrity and performance. The overarching objective of this project is to form a biomimetic membrane made of unaltered aquaporins dispersed in a polymeric membrane selective layer and capable of operation under high hydraulic pressure. To this end, polybenzimidazole (PBI) membranes were surface modified with treated aquaporins in order to achieve higher water flux and selectivity. Membranes modified with aquaporins displayed lower flux declines and higher flux recovery values after backwash as compared to unmodified PBI membranes. Also, modified membranes showed improved rejection values for both protein and salt solutions of different concentrations. However, there was leakage of ions between the channels. Therefore, in order to improve the rejection of protons, ions and other impurities, aquaporin channels were aligned with the direction of water flow. Functional groups were installed on AqpZ for covalent attachment to the polymer matrix so that the proteins could be immobilized to the membranes and aligned in the direction of the flow.

DESALINATION AND POTABLE WATER PRODUCTION I

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Modeling Low-Pressure Nanofiltration Membranes for Softening and Pretreatment.

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SMALL Flexible Reverse Osmosis System for Off-GRID Water Purification and Desalination.

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small Flexible REVERSE OSMOSIS SYSTEM for off-grid Water Purification and Deslaination

Authors: ***Tae Lee***[#], *Anditya Rahardianto, Yoram Cohen*

Chemical and Biomolecular Engineering Department and Institute of the Environment and Sustainability, Water Technology Research Center, University of California Los Angeles,

Abstract

Various remote communities around the world are confronted with impaired local water supplies. In such communities establishing and maintaining reliable distributed water treatment systems for the production of safe drinking water is a major challenge. Water treatment systems for deployment in remote communities must possess the following attributes: a) provide a physical barrier for reliable contaminant removal, b) high operational flexibility to handle geographical and temporal variability of feed water quality and other operational requirements (e.g., water recovery), c) amenable to process automation, d) compact foot-print capable for fixed or mobile deployment, and e) standardized system configuration (for ease of maintenance and operator training). In this regard, membrane-based (nanofiltration (NF) and low-pressure reverse osmosis (RO)) water treatment is most suitable for meeting the above needs. Accordingly, a novel flexible RO/NF (FRO) system platform was developed with enhanced small-system energy efficiency and high operational flexibility (allowing a wide water recovery range of 10-95%), while minimizing plant footprint. Advanced system control was implemented that enables autonomous, self-adaptive operation of FRO over a wider range of feed water salinity (e.g., 500 mg/L – 35,000 mg/L) while maintaining energy-optimal conditions. A key feature of FRO is the ability to switch (on demand) between various operational modes (e.g. batch, continuous, and semi-batch modes) depending on feed water conditions and treatment targets using a single system platform. Furthermore, the present unique FRO system design enables continuous operation (without interruptions of permeate productivity) and without the need for a typical high pressure pump (>150 psi) used in single or multi-stage RO systems. System performance was then analyzed via process models that were validated with both laboratory and field data for brackish water and sea water desalination, as well as for nitrate removal from impaired potable groundwater sources. Both experimental and modeling results demonstrated that the innovative FRO system platform allows for flexible operation over a wide range of product water recovery, while maintaining high energy efficiency (i.e., low energy consumption suitable for use with renewable energy). Therefore, FRO is particularly attractive for distributed deployment in rural or isolated communities where high water recovery is critical for various water sources of different salinity levels.

Use of Electrodeionization in Small Scale Desalination.

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Currently reverse osmosis dominates desalination because of low cost, reliability, and choices in the market place. However, there are many new deslatination opporunities, especially in brackish water application, where the size and scale make it possible to consider other technology. One of these technologies is electrodeionization. Electrodeionization is a technique in which we use wafers to remove ions to low concentration through an electricially driven process. Because the cost is related to the amount of ions being moved this technology can be cost competitive at low to medium ion concentration and low to medium scale. The purpose of this presentation is to explore places where electrodeionization can be economically feasible and show the fundamental scientific challenges with the technology.

5 A Module-Scale Computational Fluid Dynamics Model to Evaluate Hybrid Osmotically-Driven Desalination Systems.

Lori Jones *and Andrea Achilli*
Environmental Resources Engineering, Humboldt State University, Arcata, CA

7 Hybrid Pressure Retarded Osmosis-Membrane Distillation (PRO-MD) Process for Osmotic Power and Clean Water Generation.

Gang Han*, Jian Zuo, and Tai-Shung Chung*
Chemical and Biomolecular Engineering, National University of Singapore, Singapore, Singapore

9 Novel Thermal Efficiency-Based Model for Geothermal Membrane Distillation.

Johan Vanneste*, John Bush, Christopher Marks, and Tzahi Y. Cath*
Civil and Environmental Engineering, Colorado School of Mines, Golden, CO

DESALINATION AND POTABLE WATER PRODUCTION II

Water Filtration Using Naturally-Occurring Membranes in Plant Xylem.

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Low-cost, accessible, point-of-use technologies for water filtration have the potential to greatly reduce the global burden of waterborne illnesses. Drawing inspiration from fluidic transport in plants, we explored the possibility of using plant xylem tissue for low-cost water filtration. The xylem tissue conducts sap in plants and has evolved porous membranes that provide low resistance to flow while arresting the spread of cavitation-induced bubbles. We demonstrate that plant xylem in the sapwood of coniferous trees can be used to effectively remove E. coli bacteria from water at high flow rates. However, a major challenge associated with the use of xylem for water filtration is the drop in permeability and deterioration in rejection ability due to the structural changes induced during drying, which is crucial in the context of transportation and shelf-life. We have developed methods to preserve the structural integrity of the xylem and to minimize the negative impacts on filtration characteristics due to drying. Further, we found that the permeability after drying is a strong function of filter length and have studied ways to design the filter to achieve an optimal balance between flow rate and rejection ability. We have also demonstrated gravity-driven filtration through the xylem and conducted fouling studies to gain insights into filter lifetime and variation in flow characteristics over time. Fabrication of the filter is simple, and the wood required for fabrication of a gravity-driven filter with a flow rate exceeding 1 L/h costs less than 1 cent and weighs only 8 grams. This work suggests the potential of plant xylem for realizing inexpensive, locally-manufacturable, and disposable point-of-use water purification devices.

10 Development of Highly Permeable Thin Film Composite Polyamide Membranes for Water Desalination through Reverse Osmosis with Polydopamine/Molecular Sieve Particles Layer.

Pinar Cay Durgun *and Mary Laura Lind*
School for Engineering of Matter, Transport, and Energy, Arizona State University, Tempe, AZ

11 Ion and Methanol Sorption and Transport in a Cation Exchange Membrane Based on Crosslinked Sulfonated Polystyrene.

Michele Galizia[1]*, Francesco Maria Benedetti*[2]*, Donald R. Paul*[3]*, and Benny D. Freeman*[1]
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12 Controlling Water Content of Cross-Linked Polymer Membranes and Its Effect on Ion Sorption Properties.

Eui-Soung Jang[1]*, Don R. Paul*[2]*, and Benny D. Freeman*[1]

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Recent Achievements in the Zeta Potential Analysis of Membranes for Desalination.

Thomas Luxbacher[1]*, Bryan D. Coday*[2]*, Tzahi Y. Cath*[2]*, and Andriy Yaroshchuk*[3]
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Surface charge plays a major role in solute rejection and fouling of polymer membranes used for nanofiltration and reverse osmosis processes. Surface charge is accessible through the membrane zeta potential, which has gained severe interest starting in the early 1990s. Since then a variety of flat sheet membranes but also of hollow fiber membranes have been characterized in terms of the surface zeta potential.

However, what has been neglected in most of these studies was the possible influence of membrane porosity on the zeta potential. Furthermore, the majority of membrane zeta potential data was obtained by using a standard aqueous solution with an ionic strength of 0.001-0.01 mol/l. The boundary conditions for zeta potential analysis thus differ significantly from those experienced by NF and RO membranes for seawater or brackish water desalination, where the membranes are exposed to high salinity conditions.

In this contribution, we address the effects of membrane porosity and water salinity on the zeta potential analysis. Recently, evidence for the contribution of the porous membrane body to the zeta potential was confirmed for flat sheet membranes used in microfiltration. We extend the new approach, i.e., the streaming current measurement at varying distances between samples of a flat sheet membrane, to TFC NF and RO membranes. Although the nonwoven support dominates the total thickness of such membranes, we find little evidence for an influence of its porous structure.

For the second topic, we report on the impact of high ionic strengths on the membrane zeta potential. Streaming potential measurements on a TFC RO membrane were conducted in a wide range of salt concentration. Zeta potential calculated from streaming potential was then extrapolated to an environmentally relevant ionic strength (up to 1 mol/l). Results revealed that the membrane zeta potential approaches a finite equilibrium value at high salinity.

13 Environmental and Economic Assessment of Fertilizer Drawn Forward Osmosis and Nanofiltration Hybrid System for Desalination of Mine Impaired Water.

Jung Eun Kim[1], Sherub Phuntsho[1], Ko Kyong Shon[1], and Laura Chekli[2]
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DESIGN AND PROCESSING OF INORGANIC MEMBRANES

Development of Zeolite Membrane Products in a Thin Sheet Form.

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Developing low-cost zeolite membranes is important for a range of industrial applications. In this presentation, design principles and preparation methods of zeolite membranes in a thin-sheet form will be introduced. A zeolite membrane layer is directly grown on a flexible, 50µm-thin metal support sheet with strong adhesion and without defects. The resulting zeolite membrane sheet has mechanical flexibility and strength like a thin metal sheet. The new membrane product development will be elaborated with NaA-type, MFI-type, and Faujasite-type zeolite frameworks – the three commonly-used zeolite materials. Characterization results of micro-structures and molecular sieving functions will be discussed. These thin zeolite membrane sheets show excellent gas and molecular separation performances, such as air dehumidification, alcohol dehydration, CO_2 separation, and ethanol enrichment. The thin membrane sheet makes it possible to achieve low-cost, high throughput production and to make zeolite membrane modules of membrane area packing density comparable to polymeric membrane sheets.

Highly Permeable N_2/CH_4 Separation SAPO-34 Membranes Synthesized By Diluted Gels and Increased Crystallization Temperature.

Zhaowang Zong[1]*, Xuhui Feng*[1]*, Yi Huang*[2]*, Zhuonan Song*[2]*, Rongfei Zhou*[3]*, Shaojun James Zhou*[4]*, Moises Carreon*[1]*, Miao Yu*[5]*, and Shiguang Li*[4]
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Synthesis conditions were optimized for synthesizing SAPO-34 membranes towards N_2/CH_4 separation. Compared to previous SAPO-34 membrane preparations, synthesis gels were diluted 1.3–2.7 times and an increased crystallization temperature was used. As a result, a 3–4 fold increase in N_2 permeance was observed in this study. The membranes separated N_2 from CH_4 with N_2 permeance as high as 1300 GPU and selectivity of 7.4 at 23 °C for a 50/50 N_2/CH_4 mixture. Furthermore, membranes were reproducible and effectively separated gas mixtures having low N_2 content which are relevant compositions of natural gas. More specifically, membranes separated N_2 from CH_4 with N_2 permeance as high as 1160 GPU and selectivity of 7.1 at 23 °C for an 18.5/81.5 N_2/CH_4 mixture. The resultant SAPO-34 membranes have potential for economic N_2 rejection in natural gas processing.

15 **Macro-Porous Alpha-Alumina Support Tubes for Thin Defect-Free Membranes, Made By Centrifugal Colloidal Casting.**

Ralph Bauer
Department of Materials Science and Engineering, The Ohio State University, Columbus, OH

N/A **Fabrication of CNT Hollow Fiber Membranes and Its Applications.**

Heeyoung Kim
Civil and Environmental Engineering, KAIST, □□, Korea, Republic of (South)

16 **Large-Area Fabrication of Graphene-Based Membranes By Shear Alignment of Discotic Nematic Liquid Crystals of Graphene Oxide.**

Abozar Akbari[1], *Dibakar Bhattacharyya*[2], *and Mainak Majumder*[1]
(1)Mechanical and Aerospace Engineering, Monash University, Clayton, Australia, (2)Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY

17 **Nitrogen Selectivity of Molybdenum Metallic Membranes.**

Kyoungjin Lee[1], *Simona Liguori*[1], *Ralph Bauer*[2], *Hendrik Verweij*[2], *and Jennifer Wilcox*[1]
(1)Department of Energy Resources Engineering, Stanford University, Stanford, CA, (2)Department of Materials Science and Engineering, The Ohio State University, Columbus, OH

19 **Process Design of Natural Gas Treatment Using DDR-Type Zeolite Membrane.**

Hiroaki Hasegawa[1], ***Keiichi Nishida***[1], *Shuichi Oguro*[1], *Yasushi Fujimura*[1], *Kenji Yajima*[2], *Makiko Niino*[2], *Manabu Isomura*[2], *and Toshihiro Tomita*[2]
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DESIGN AND PROCESSING OF POLYMERIC AND ORGANIC MEMBRANES II

Electrospun Nanofiber Membranes for Water Treatment and Reuse.

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Water treatment and reuse is becoming an increasingly important issue for all regions of the world regardless of their level of water abundance or aridity. Membrane technology has provided a versatile platform for developing a host of water treatment technologies that enable us to tap sources for water that only decades ago would have never been considered as viable sources of water (seawater, produced water, wastewater). Continued innovation in the water treatment membrane field continues today as new materials are sought that leverage important structure-property relationships that push the barrier of membrane performance. One material in particular, nanofiber nonwovens, has recently achieved attention as a possible platform for improving membrane performance because of their intrinsically high permeability, low resistance to mass transfer, and high surface area. In our work, we explore the use of polymer nanofiber nonwovens made through electrospinning for use across a wide range of membrane applications. These include:

- *Electrospun supported thin film composite membranes for forward osmosis (FO):* Electrospun materials are demonstrated to have excellent mass transfer properties which reduce resistances to solute transfer in forward osmosis.

- *Nanofiber membranes for membrane distillation (MD):* Electrospun nonwovens have properties of high porosity and small pore size, making them suitable for MD applications. We demonstrate high flux performance of these membranes under very modest temperature gradients using high salinity feeds.
- *High surface area activated carbons:* Using electrospun precursors, we have established protocols for making high surface area carbon materials in a nonwoven configuration that are appropriate for organic removal in sorption applications.
- *Use of commercial nanofiber materials for membrane applications:* We have explored the use of commercial nanofiber nonwovens from DuPont in both FO and MD applications. This demonstrates that commercial nanofiber nonwovens, which are made roll-to-roll, are applicable to these emergent membrane disciplines. Availability of these materials commercially could aid in commercialization efforts.

In all, this work demonstrates the promise of using nanofibers across a number of key membrane disciplines in the water treatment space.

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A New Method of Fabricating Charge Mosaic Membranes By Inkjet Printing.

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Thin-Film Composite Membranes with Regular, Sub-Micron Surface Patterns: Fabrication and Characterization.

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Carbon Nanotube Multilayer Polyelectrolyte Charge Mosaic Membranes.

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Robust Outer-Selective Thin-Film Composite Polyethersulfone Hollow Fiber Membranes with Low Reverse Salt Flux for Renewable Salinity-Gradient Energy Generation.

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This study reports outer-selective thin-film composite (TFC) hollow fiber membranes with extremely low reverse salt fluxes and robustness for harvesting salinity-gradient energy from pressure retarded osmosis (PRO) processes. Almost defect-free polyamide layers with impressive low salt permeabilities were synthesized on top of robust polyethersulfone porous supports. The newly developed TFC-II membrane shows a maximum power density of 7.81 W m^{-2} using 1 M NaCl and DI water as feeds at 20 bar. Reproducible data obtained in the 2^{nd} and 3^{rd} runs confirm its stability under high hydraulic pressure differences. Comparing to other PRO membranes reported in the literature, the newly developed membrane exhibits not only the smallest slope between water flux decline and ΔP increase but also the lowest ratio of reverse salt flux to water flux. Thus, the effective osmotic driving force could be well maintained even under high pressure operations. For the first time, the effect of feed pressure buildup induced by feed flowrate was evaluated towards PRO performance. A slight increment in feed pressure buildup was found to be beneficial to water flux and power density up to 10.06 W m^{-2} without comprising the reverse salt flux. We believe this study may open up new perspectives on outer-selective PRO hollow fiber membranes and provide useful insights to understand and design next-generation outer-selective TFC hollow fiber membranes for osmotic power generation.

Elucidating the Reverse Osmosis Polyamide Formation Mechanism from Pseudo-Stop-Motion Imaging.

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(1)R&D, Dow Water & Process Solutions, Edina, MN, (2)The Dow Chemical Company, Edina, MN

The formation mechanism of reverse osmosis polyamide membranes has long eluded the scientific community, primarily due to an inability to observe the formation, which occurs both too quickly and on too small a scale. Extensive data has been gathered over the years to understand the effects of recipe and processing conditions on the performance of these membranes, but as the technology approaches performance limits, understanding the intricacies of film synthesis may be the key to fine-tuning an established chemistry to maximize separation efficiency.

For the first time, methods of freezing in time polyamide at various stages of formation have been developed. Custom-designed casting and imaging methods provide a pseudo-stop-motion view of polyamide film growth and insight into the forces that lead to the typical polyp structures of RO membranes. The structures have been shown to be much less random than they appear, and through well-controlled pilot-scale membrane manufacturing have been manipulated to illustrate a new mechanistic theory.

Evidence of a relationship between structure and parameters such as interfacial tension, amine pK_a and temperature will be presented. Further evidence based on manipulation of downstream process conditions solidifies the argument for a "balloon inflation" growth mechanism. This evidence will be presented in the context of three common polyamide structures along with application to the future of reverse osmosis membrane development.

26 Facilitated Transport Membranes in the Solid State Containing Surface-Activated Ag Nanoparticles for Olefin/Paraffin Separation.

*Young Rae Kim, Gi Hyeon Moon, and **Yong Soo Kang***
Energy Engineering, Hanyang University, Seoul, Korea, Republic of (South)

DESIGN AND PROCESSING OF POLYMERIC AND ORGANIC MEMBRANES III

Plasticization of Glassy Polymeric Membranes in Gas Separations: Assessment and Prediction.

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The permeability behavior of glassy membranes as upstream pressure increases shows different trends, including the monotonous decline, a monotonous increase, as well as an initial decline followed by a subsequent increase after a minimum permeability value is reached. The minimum value, whenever present, occurs at a pressure conventionally indicated as the plasticization pressure. The plasticization phenomenon has not been inspected in detail thus far, in terms of material property variations; current physical interpretation associates to the plasticization pressure the onset of a generic softening of the polymer matrix, which is considered responsible of the observed increase in permeability and decrease in selectivity.

On the other hand, by considering several different glassy membranes we have observed that the different behaviors observed for gas permeability can be described by considering only a solution-diffusion model in which molecular mobility varies with penetrant concentration through an exponential law, with two adjustable parameters only. Diffusivity is taken as the product of molecular mobility and a thermodynamic factor, which is calculated by using the NELF model for thermodynamic properties of the glassy phase.

It is observed that by fitting the only two adjustable parameters of the model to the initial branch of the permeability-pressure curve it is possible to predict the plasticization pressure, if existing, by using only the solubility diffusivity model without introducing any additional physical phenomenon.

The agreement observed between model calculations and experimental data of CO_2 permeability in various glassy polymers is very satisfactory. That allow us to offer a deeper insight on the so-called plasticization phenomenon. By considering at the same time the permeability isotherm, the solubility isotherm and the concentration and swelling profiles in the membrane, we can show that in some cases the plasticization pressure takes place after part of the membrane has turned into rubbery phase; while in other cases, e.g. for Matrimid polyimide, plasticization pressure takes place when the entire membrane is still glassy but with a polymer swelling sufficient for a permeability increase.

Finally, it is observed that all parameters used have a defined physical meaning which lead to good general correlations with both polymer and penetrant properties, based on which permeability predictions can be obtained.

Solvent and Thermal History Effects on Gas Transport in TR Polymers and Their Precursors.

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HAB-6FDA polyimide was synthesized by a two-step polycondensation method with chemical imidization. Dense polymer films were solution cast from tetrahydrofuran (THF), acetone, and N,N-dimethylacedamide (DMAc). Films cast from THF and acetone were cast in a solvent saturated glove bag then dried at 200°C for 24 h. Two separate films were cast from DMAc in a vacuum oven using different heating and vacuum protocols, with one utilizing a gas purge and the other a temperature ramp under partial vacuum. Each precursor film was used to prepare thermally rearranged (TR) polymers. The rearrangement reaction was performed at 400°C and resulted in a 54% conversion to the polybenzoxazole TR product. Pure CH_4 and CO_2 gas permeability measurements were made on both the precursor and the TR polymer. While the ideal CH_4/CO_2 selectivity remained constant for all four polyimide films, the different casting procedures resulted in a 40% difference in permeability coefficients, with the film prepared from DMAc under partial vacuum having the lowest permeability coefficients for both gases and the DMAc film cast using a gas purge having the highest. The respective TR polymer films exhibited the same trend in permeability with a 37% variation with only minimal differences in selectivity. These trends have been attributed free volume variations due to the different casting techniques and the inability to thermally "reset" the history of the polyimide precursor.

Molecular Design of Nanofiltration Membranes for the Recovery of Phosphorus from Urban Wastewater.

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With the rapid depletion of mineral phosphorus, the recovery of phosphorus from sewage sludge will become increasingly important in the near future. However, the presence of various contaminants such as heavy metals in the sewage sludge only serves to complicate the issue, and the challenge lies in the separation of phosphorus from the heavy metals to produce fertilizers of high quality. Among various available methods, nanofiltration (NF) has been demonstrated to be a feasible and promising option when the sewage sludge undergoes acidic dissolution (pH <2). Since the performance of commercially available thin film composite (TFC) NF membranes reported thus far has great rooms for improvement, the development of highly permeable positively charged NF membranes are recommended. To this aim, a NF membrane which is desirable for phosphorus recovery was fabricated via interfacial polymerization of polyethyleneimine (PEI) and trimesoyl chloride (TMC) on a porous polyethersulfone (PES) membrane substrate. Through an optimization of the interfacial polymerization process which involves varying the molecular weight of PEI and the concentration of TMC, the resultant membrane displays a low molecular weight cut-off (MWCO) of 170 Da with a reasonably high pure water permeability (A) of 6.4 LMH/bar. The newly developed NF membrane can effectively reject a wide variety of heavy metal ions such as Cu, Zn, Pb and Ni (>93%) while demonstrating a low phosphorus rejection of 19.6% at 10 bar using a feed solution of pH 2. Thus, up to 92% of the feed phosphorus may be recovered using this newly developed NF membrane at a permeate recovery of 90%. This is a highly competitive value for the recovery of phosphorus.

Interfacial Polymerization for Sugar / Ionic Liquid Separations.

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Ionic Liquids (IL) are tunable green solvents for a variety of chemical and biochemical processes. However, the economic viability of utilizing these green solvents depends on developing processes for their recycle and reuse. ILs are outstanding solvents for biomass fractionation and sugar conversion processes. However, separating saccharides from ILs is generally very difficult due to the similarity of their molecular weight. Here a selective skin layer containing 3-aminophenylboronic acid has been successfully synthesized via interfacial polymerization on the surface of asymmetric polyethersulfone (PES) membranes. The fabricated composite membranes show superior ionic liquid/sugar selectivity at competitive permeability. Moreover, the selectivity can be tuned by varying the monomer composition, the polymerization time and post treatment conditions. While [EMIM]Cl and [BMIM]Cl are able to selectively permeate through the membranes, over 90% of mono- and oligosaccharides are rejected. The compositional, chemical and morphological properties of these nanofiltration membranes are characterized and correlated with their separation characteristics.

Organic Solvent Nanofiltration with Novel Polymeric Membranes.

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A very large variety of membranes polymeric or otherwise have been investigated over the last two decades for organic solvent nanofiltration (OSN). The materials and structures used to make OSN membranes include among others the following: poly (dimethylsiloxane) (PDMS); mixed matrix membranes (MMMs) of PDMS with zeolites and other fillers; asymmetric integrally skinned polyimide (PI) membrane crosslinked with aromatic or aliphatic diamines; polyaniline; polypyrrole; interfacially polymerized polyamide w/o carbon nanotubes; carbon-based membranes including graphene. One of the weaknesses of most polymeric membranes is their varying tendencies for swelling with demanding organic solvents aprotic or otherwise; this gets reflected in the solute rejection behaviors of such polymers. To this end we have started studying membranes from a particular class of polymers for OSN. We report preliminary results of solvent flux and solute rejection for such membranes. We also report results of molecular dynamic simulations of transport in one such polymeric membrane.

27 Comparison of Performance Between Laboratory Scale and Industrial Scale Membranes.

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DESIGN AND PROCESSING OF POLYMERIC AND ORGANIC MEMBRANES I

Manipulating Nanopore Selectivity in Lyotropic Liquid Crystal Polymer Nanofiltration Membranes for the Recovery of Targeted Organic Solutes.

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Polymeric Micro-Spherical Particles Grafted on Water Treatment Membranes: Mechanism of Formation and Applications.

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Surface Characterization of Membrane Surfaces Nanostructured with Tethered Hydrophilic Polymers.

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Membrane surface modification with end-tethered hydrophilic polymers is an effective approach for reducing fouling propensity and improving cleaning efficiency of RO and

UF membranes. It has been suggested that, in addition to chemistry, swelling of the polymer layers play a crucial role in minimizing foulant attachment, yet detailed characterization of swollen tethered polymer chains is still needed in order to elucidate the mechanism by which swelling minimizes fouling. In this study, AFM was used to characterize swelling of surface tethered polymer chains by utilizing poly(acrylic acid) (PAAc) and poly(2-hydroxyethyl methacrylate) (PHEMA) chains end-grafted onto polysulfone (PSf) membrane surrogate surfaces via atmospheric pressure plasma-induced graft polymerization (APPIGP). Impact of polymer chain swelling on surface topography of PAAc and PHEMA layers was evaluated by AFM imaging in various solvents (i.e., air, deionized water, saline water). The thickness (or extension) of the swollen polymer chains was assessed by determining contour length distributions of the tethered polymer chains via single molecule force spectroscopy performed in aqueous solutions of different salinity. The adhesion force measurements were performed with a functionalized colloidal probe in order to quantify fouling potential of the polymer layers of different swelling degrees. The results of the present study provide a direct measure of the potential effectiveness of tethered chains for membrane fouling reduction. In this regard, direct surface force measurement can guide the optimization of surface modification for synthesizing high performance low fouling membranes.

Assessing Biofouling Resistance of a Polyamide Reverse Osmosis Membrane Surface-Modified with a Zwitterionic Polymer.

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Reverse osmosis (RO) is a technology that can help increase clean water supply in today's world. However, mitigation of biofouling of RO membranes is a remaining challenge towards a wider use of this technology. It was suggested that a promising way to control membrane biofouling could be surface modification, e g., using low-fouling zwitterionic polymers. Published studies demonstrated that zwitterionic coatings can indeed improve the resistance of polyamide (PA) membranes to the initial bacteria adhesion, however, no long-term experiments with real water effluents were conducted. In this report a commercial PA RO membrane was surface-modified with a zwitterionic polymer and its propensity to biofouling was tested in both short-term bacteria adhesion experiments and longer filtration tests conducted using real treated wastewater effluents spiked with a small level of nutrients. The obtained results showed that, initially, there was a clear improvement in the biofouling resistance of the modified membranes and their permeation flux remained stable, in contrast to the non-modified counterpart. However, eventually, the permeabilities of the two membranes declined to a similar degree. The results indicate that antifouling coatings might not promise a better

membrane performance in long term. The analysis of the biofilms grown on the pristine and the modified membranes suggested that adaptation capabilities of biofilms overcame the favorable changes in surface properties of the membrane achieved by the modification. The presented results emphasized the importance of long-term filtration experiments as an ultimate test for assessing biofouling resistance of the modified desalination membranes.

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UV and EB Cross-Linked Polysulfone Based Membranes for Versatile Applications.

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Design of Hydrophilic Conductive MD Membranes for Fouling Mitigation, and Direct Surface Heating.

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Membrane distillation (MD) is promising technique for treatment of waters contaminated with high salt concentration, such as ground water, produced water, and brines generated from desalination. Like all membrane processes, MD suffers from fouling that leads to performance degradation. The hydrophobic nature of the MD membrane surface allows for adsorption of NOM and other organic foulants that clog membrane pores, and can lead to membrane wetting, irreversibly degrading their performance. Here, we present a method of synthesizing composite MD membranes with hydrophilic or hydrophobic conductive carbon nanotube thin film surfaces layered on a hydrophobic MD support. We demonstrate that the hydrophilic surface reduces fouling caused by humic acids, while still maintaining the same performance as a bare MD membrane. Finally, we demonstrate a novel method of generating the thermal driving force in the MD process by heating the carbon nanotube thin film surface directly via joule heating. The direct heating of the MD surface eliminates the need to heat the bulk feed solution, allows for high recovery in single pass, and could significantly reduce the complexity and construction cost of MD plants.

DESIGNS AND PROCESSING OF COMPOSITE AND HYBRID MEMBRANES I

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Development of a Composite Membrane with a Liquid-Barrier Chemical-Resistant Polymer Matrix to Recover Water from Urine-Containing Wastewater.

Afsaneh Khosravi[1], *Andrew Dopilka*[2], *Katelyn Kline*[3], *and Mary Laura Lind*[1]

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32 **How to Enhance ZIF-8 Growth on Polymers?.**

Eva Barankova, *Xiaoyu Tan, Pradeep Neelakanda, Mahendra Kumar, and Klaus Viktor Peinemann Sr.*
AMPM, KAUST, Thuwal, Saudi Arabia

33 **Mixed-Matrix Membranes Containing Engineered Nanoporous Materials for Biogas Purification.**

Tae-Hyun Bae
Chemical and Biomedical Engineering, Nanyang Technological University, Singapore, Singapore; School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore, Singapore

35 **Metal-Rich Polymer Membranes By Cips: From Metal Ions to Crystals.**

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36 **The Enhanced Performance of Iron-Oxide and Silica-Coated-Iron-Oxide Nanocomposite Membranes during the Filtration of Oily Emulsion.**

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Porous Solid Supports for Dual-Phase Liquid/Solid Membranes.

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Dual phase membranes consisting of a liquid phase contained within a solid support show promise in a variety of applications including high-temperature CO2 separations and fuel cells. The solid support phase can simply host the active liquid phase or can participate in the separation by supplying electrons or ions. In many cases, the solid material must be inert to corrosive chemical environments at high temperature, while the pore morphology and material properties need to be optimized to suit the particular application. Lawrence Livermore National Laboratory has developed expertise in the synthesis of novel porous materials over the last four decades. These efforts have mainly focused on creating ultra-low-density carbon, metal-oxide, and inorganic materials, but recently we have turned our attention to creating support materials for molten-salt-based CO2 separation membranes. This contribution will highlight our recent developments in this area.

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37 Sub–10 Nm Polyamide Nanofilms with Ultrafast Solvent Transport for Molecular Separation.

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DESIGNS AND PROCESSING OF COMPOSITE AND HYBRID MEMBRANES II

Electrospun Composite Bipolar Membranes.

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Bipolar membranes, typically a laminate of an anion-exchange and cation-exchange membrane, have the unique capability to split water at a potential as low as 0.8 V while conventional electrolysis requires at least 1.2 V. Such membranes are employed in a number of important industrial processes, including the production of mineral acids, the recovery of organic acids from fermentation processes, pH control, and ion-exchange resin regeneration. The use of bipolar membranes in electrodialysis separations eliminates unwanted salt efflux and disposal problems and offers significant savings in electrical energy consumption. Recently, bipolar membranes have also been examined for use in self-humidifying hydrogen/air fuel cells, where the recombination of electrochemically generated hydroxide ions and protons at the bipolar junction produces water that improves membrane hydration, with higher power output at reduced feed gas humidity conditions.

We report here for the first time on the design, fabrication, and testing of a new bipolar membrane that was made by polymer nanofiber electrospinning, where the anion-exchange polymer is quaternized poly(phenylene oxide) and the cation-exchange polymer is sulfonated poly(etherether ketone). These films have an increased interfacial area for water splitting at the junction of anion and cation exchange polymers. This morphology is important for two reasons: (1) it improves the attachment (adhesion) of the two ion-exchange layers so that ballooning/delamination is minimized or eliminated and (2) the increased bipolar junction surface area will lead to a better distribution of the water splitting reaction and lower membrane voltage drop for the same operating current density. The procedure for membrane fabrication will be described and the performance of electrospun films will be compared to bipolar membranes in the literature.

Influence of Nanoparticle Processing on PES Casting Solution Viscosity.

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Nanoparticle incorporation into porous polymeric membranes has received continued attention with the concurrent continued development of reactive metallic and metal oxide nanoparticles for water treatment applications. Nanoparticles comprised of metals such as iron, nickel, palladium, silver, aluminum, and copper have been shown to remove both organic and inorganic water contaminants, and novel multi-metallic nanoparticle combinations and morphologies continue to be reported. Iron nanoparticles (Fe NPs) remain at the forefront of efforts focused on water remediation due to the low cost of the metal and the versatility of Fe NPs in addressing a wide variety of water contaminants. The incorporation of these nanoparticle materials into a support material such as a polymeric membrane immobilizes the nanoparticles, preventing movement within the treatment system, and may also provide enhanced contaminant removal. In particular, there is an interest in embedding nanoparticles in phase inversion polymeric membranes, where the nanoparticles can be incorporated into the membrane casting solution and retained in the solid membrane phase when the membrane polymer precipitates.

In this work, the incorporation of iron nanoparticles in a polyethersulfone membrane was studied. Nanoparticle stabilizer type, casting solution additives, and nanoparticle processing by centrifugal or magnetic separation were varied, and specific membrane characteristics were evaluated. Specifically, membrane casting solution viscosity, cast membrane thickness, pure water flux, and internal morphology were evaluated. While the addition of the additives ethanol and polyvinylpyrrolidone to a polyethersulfone-dimethylacetamide solution causes an expected increase in viscosity, the addition of nanoparticles can cause an increase or decrease in viscosity depending on the ligand stabilizer used during nanoparticle synthesis and casting solution additive concentration. Viscosity can also be affected by nanoparticle separation method, but again, changes are also dependent on casting solution composition. Varying changes in membrane thickness are observed and can be correlated to viscosity. Pure water flux decreases for all samples when nanoparticles are added, but the extent of the change is affected by casting solution composition. Internal morphology can partially explain the decrease in flux for nanoparticle-embedded membranes.

Membrane Separation of CO2 from Syngas Using PDMS and Mixed Matrix Membranes Oral.

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Carbon dioxide (CO_2), being one of the leading global greenhouse gas emissions, can be important to remove from other gaseous components in downstream processing. In processes such as gasification or dry CH_4 reforming, CO_2 along with syngas (CO and H_2) are the primary products. In order for syngas to be used in other processes, such conversion into methanol or ammonia, these components must be separated. Polymeric membranes have been proven to selectively separate CO_2 over syngas, due to the favoured transport mechanism. Along with these materials, mixed matrix membranes are also proving to be novelty separation methods, combining the adsorption and membrane separation mechanisms to further improve their performances. In this study, commercial pure PDMS membranes, along with PDMS mixed matrix membranes including activated carbon and zeolites were investigated for CO_2 removal from syngas

38 Iron Nanoparticle Functionalized Membrane for PCB Degradation from Water.

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39 Novel Supra-Molecular Organic Framework (SOF) Based Mixed Matrix Membranes (MMMs) for CO2/CH4 Separation.

Zoban V. Singh[1]*, Richard Noble*[1]*, Douglas L. Gin*[1]*, Wei Zhang*[2]*, LiLi Tan*[2]*, and Matthew G. Cowan*[3]
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40 Fouling Control Using Temperature Responsive Membranes Activated Using Superparamagnetic Iron Oxide Nanoparticles.

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41 Tuning the Carboxylic Groups of the Thin-Film Composite Membranes and Their Effects on the Performance.

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43 **Extended Field Trials of Sweep Modules for Carbon Capture with Flue Gas from a Power Plant.**

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ENERGY APPLICATIONS (FUEL CELLS, BATTERIES, BUILDINGS)

44 **Analysis of Flux Reduction Behaviors of PRO Hollow Fiber Membranes: Experiments, Mechanisms, and Implications.**

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Membranes for Air-to-Air Water Vapor Exchangers.

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Energy recovery ventilation (ERV) is an emerging application for polymeric membranes used in energy efficient building ventilation systems. In these enthalpy exchange devices, heat and moisture are transported through a membrane between fresh supply ventilation air streams and stale building exhaust air streams. Membranes for these devices must have high water vapor permeance and good selectivity of water vapour over indoor air contaminants.

This presentation will discuss ongoing membrane research and development efforts at dPoint Technologies. Experimental results on multi-layer membrane structures based on several substrate platforms are presented, demonstrating the contribution of substrate and selective layer resistances to transport in these air-to-air transport devices. Several selective layer polymers are also discussed and results are reported in terms of water vapour permeability and selectivity for water vapour over gases and volatile organic

compounds. The thermal effects on permeability in these polymers and interactions of water and water vapour with these polymers are also discussed. Specifically development of the "Gryphon" series of membranes will be discussed, these blended membranes are designed to have low VOC transport under humid air conditions. Results from mixed gas studies demonstrate how high humidity impacts selectivity when using various polymers. Focus areas for future membrane, exchanger, and process research will be discussed.

46 Highly Proton-Conductive Polyelectrolyte Membranes with Greatly Reduced Water Swelling.

Joseph Aboki, Shuangjiang Luo, and ***Ruilan Guo***
Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN

47 Polymer Blend Electrolyte Membrane Containing Hydroxyl Group for Long Term Durable Proton Exchange Membrane.

Bo Hyun Kim[1,2]*, So Young Lee*[1]*, Jong Hyun Jang*[1]*, Dirk Henkensmeier*[1]*, Sung Jong Yoo*[1]*, Ki Wan Bong*[2]*, and Hyoung-Juhn Kim*[1]
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Graphene Quantum Dot Sensitization and Nitrogen Doping of Ordered Mesoporous TiO2 Thin Films for Visible Light Driven Water Splitting.

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The optical and electronic properties of TiO_2 thin films provide tremendous opportunities in several applications including photocatalysis, photovoltaics and photoconductors for energy production. Despite many attractive features of TiO_2, critical challenges include the innate inability of TiO_2 to absorb visible light and the fast recombination of photoexcited charge carriers. In this study, we prepared ordered mesoporous TiO_2 films co-modified by graphene quantum dot sensitization and nitrogen doping (GQD-N-TiO_2) for hydrogen production from photoelectrochemical water splitting under visible light irradiation. First, cubic ordered mesoporous TiO_2 films were prepared by a surfactant templated sol-gel method. Then, TiO_2 films were treated with N_2/Ar plasma for the incorporation of substitutional N atoms into the lattice of TiO_2. GQDs were prepared by chemically oxidizing carbon nano-onions. The immobilization of GQDs was accomplished by reacting carboxyl groups of GQDs with amine groups of N-TiO_2 developed by the prior immobilization of (3-aminopropyl)triethoxysilane (APTES). Successful immobilization of GQDs onto N-TiO_2 was probed by UV-Vis, FT-IR, zeta potential and contact angle measurements. The nitrogen-doped TiO_2 (N-TiO_2) showed the significant reduction of band-gap (3.5 eV to 2.88 eV) and the unprecedented enhancement (240 times) of photocatalytic hydrogen production visible light illumination. The GQD-immobilized N-TiO_2 film showed about 2 times enhancement compared to N-TiO_2, showing the important role of GQDs. This outstanding enhancement is attributed to the high surface area of mesoporous films and synergistic effects of nitrogen doping and GQD sensitization resulting in enhanced visible light absorption, efficient charge separation and transport.

48 Application of Trimethylamine–Carbon Dioxide in Osmotic Heat Engine for Power Generation.

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ENVIRONMENTAL EMISSION CONTROLS

Present Situation of Air Pollution and Control Strategy in China.

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For recent years, people in most northern and eastern parts of China have suffered from the heavily polluted haze. Besides natural climate variations, emissions from transportation and industrial sources have been the main contributors. In this presentation, current situation of industrial air pollution emissions in China will be summarized and applications of pollution control technologies will be critically reviewed with emphasis on the catalytic oxidation of volatile organic compounds (VOCs) and potential opportunities for porous ceramic membrane filters.

Post-Combustion Flue Gas Separation Membrane Performance Testing Skid.

Victor A. Kusuma[1], *Surendar Venna*[2], *Ganpat J. Dahe*[1], *Shan Wickramanayake*[3], *Kevin P. Resnik*[4], *David Hopkinson*[5], *and Christina Myers*[6]

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We have recently constructed and deployed a constant pressure/variable volume membrane gas separation performance testing system at the National Carbon Capture Center (NCCC). The skid-mounted system was intended to perform fully automated testing of bench-scale experimental membranes using real flue gas obtained from Alabama Power's Gaston Unit 5, a pulverized coal fired boiler. Currently the unit is optimized to deliver up to 50 cc/min flue gas at up to 2 bar to small membrane samples (around 2 cm^2 in area) in both hollow fiber and flat sheet form, but the unit itself is amenable to future upgrades to test larger membrane modules. In this talk, we will present the unit's capabilities and share some preliminary results from testing several mixed matrix thin film composite hollow fiber membranes on actual flue gas with humidity and minor contaminants present. These lab-scale membranes were tested over short testing periods, quantifying the carbon dioxide, oxygen, nitrogen and water vapor permeances, and we expect to continue testing more membranes over longer periods during the summer.

N/A

The Removal of Elmental Mercury from Flue Gas By Different Materials.

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Dust-Removal Technique Combined with Dust Pre-Charge and Electric Ceramic Tubes Loaded with High Voltage.

Haidi Liu
State loboraotry of multiphase complex system, The Institute of Process Engineering, CAS, Beijing, China

Abstract:A new dust elimination technique combined with dust pre-charge and electric ceramic tubes loaded with high voltage was investigated. During the operation of this technique, the dust was firstly pre-charged by pre-charge appliance with DC negative corona (-20 kV), and then the gas containing dust was forced to penetrated the wall of porous electric ceramic tubes loaded with negative high voltage (-5000 V) to undergo dust elimination. It was revealed by the results that, this new technique obviously decreased the pressure drop of the ceramic tubes during the de-dust process. With the new technique, the increasing speed of the pressure drop was only 0.18 times to that with

normal technique in same conditions during the same operation time. The increasing speed of the pressure drop under the new technique was only 0.29 times to that with normal technique in same conditions under the same dust layer mass. The results were high possibly caused by the fact that the electrostatic repulsion force between the dust particles gives rise to loosely compacted dust layer, furthermore, the electrostatic repulsion between the electric porous ceramic tubes and the pre-charged dust particles bring about very loose attachment between the dust layer and tube surface, as a result, the dust layer was easy to remove and its pressure drop was greatly decreased. This new technique was expected to obviously reduce the pressure drop of ceramic tube in industrial de-dust operation, and prolong its regeneration period.

Preparation and Application of Ceramic Membranes for Hot Metallurgical Gas Cleaning.

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Alumina-based ceramic filtration membranes were prepared on a large-pore silicon carbide supports using alumina and mullite particles as the raw materials by spray-coating, followed by dip-coating for modification. The preparation process, including the powder pre-treatment, the formation and sintering of membranes, was systematically studied. Optimization of the raw materials ratio was found to be necessary to avoid crack forming during sintering and application. The microstructure, pore properties and gas permeation flux of prepared membranes were investigated. The preferred sintering temperature for the membranes was in the range of 1190–1220 °C based on the results of SEM, pore-structure and pressure drop. Low cost alumina-based membrane tubes with average pore size 6.7μm and pressure drop of 470Pa under the filtration velocity of 1 m/s were obtained. The length, outer diameter, and wall thickness of the membrane tubes were 1600mm, 60 mm and 10 mm, respectively. A dust filter equipped with 1760 resulting membrane tubes (capacity:45000Nm^3/h) was built at Huaian Special Steels (East China) to clean metallurgical sintering flue gas. Efficiencies of filtration of sintering flue gas were found to be greater than 99.95% which gave rise to very low dust content in the outlet fume gas (<10 mg/Nm^3). These results make the ceramic membrane filter very promising for hot and corrosive industrial exhaust gas filtration applications.

Functionalized Cellulose Nanofiber Membranes for Heavy Metals Removal from Impaired Water.

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In this project, high-performance, nanofiber-based ion-exchange membranes were prepared for removal of heavy metals from impaired waters. Our hypothesis was that such membranes would have high metal ion capacities resulting from large surface area-to-volume ratios and high water permeability relative to barrier-type membranes such as reverse osmosis and nanofiltration. The nanofiber membranes were produced by electrospinning cellulose acetate nanofiber mats, which were strengthened by thermal-mechanical annealing and then converted to regenerated cellulose nanofiber mats. Subsequent surface modification transformed the membranes into ion-exchange membranes for removal of trace metal ions in water.

Cellulose acetate was selected as the starting material because it has been used widely to electrospin fibers due to simple processing. The electrospinning formulation and conditions yielded fiber mats having a fiber diameter in submicron range and a thickness range of 160 to 330 μm. Following annealing, the nanofiber mats were converted to regenerated cellulose, which is a low-fouling material that can be modified using convenient surface chemistry to introduce the ion-exchange ligands.

Ion exchange using carboxylate anion ligands is a potential strategy to capture cadmium and nickel ions found in industrial wastewaters. Thus, the regenerated cellulose nanofiber mats were modified by grafting poly(itaconic acid) (dicarboxylic acid side groups) and poly(acrylic acid) (monocarboxylic acid side groups) to the surfaces of individual nanofibers that had been modified with poly(glycidyl methacrylate).The success of poly(itaconic acid) and poly(acrylic acid) grafting was confirmed by attenuated total reflectance Fourier-transform infrared spectroscopy.

Direct-flow filtration measurements showed that the nanofiber membranes have water permeabilities of 400-1600 L/m^2/bar/h, much higher than reverse osmosis or nanofiltration membranes. The single-component ion-exchange isotherms were measured at constant pH for cadmium, nickel, and calcium ions. Competitive sorption measurements were made using environmentally relevant concentrations of these ions to determine the selectivity of the membranes for cadmium ions. Experimental isotherms for Cd-Ca and Cd-Ni were compared to model predictions. The multi-component isotherms for Cd-Ca and Cd-Ni systems were modeled using the competitive Langmuir model with Langmuir parameters obtained by fitting single-component isotherms.

Results show that the polymer-modified nanofiber membranes have outstanding permeability and high selectivity for heavy metals over a common competing anion present at much higher concentration. The nanofiber membrane adsorbers bind cadmium ions with static capacities that are similar to and, in some cases, superior to commercial ion-exchange resins and activated carbon.

50 Photocatalytic Membrane Reactors for High Throughput Virus Removal and Inactivation.

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GAS SEPARATION I - NOVEL MEMBRANE MATERIALS

Preparation and Characterization of a Hydrophobic Metal-Organic Framework Membrane.

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A hydrophobic metal-organic framework (MOF) UiO-66-CH_3 is prepared and its solvothermal stability is investigated in comparison to UiO-66. It is confirmed that the MOF stability is enhanced by introduction of the two methyl groups, while the water adsorption is reduced. Given its hydrophobicity and stability, UiO-66-CH_3 is proposed as an attractive membrane material for gas separation under moisture conditions. The UiO-66-CH_3 membrane is prepared on a 50µm-thick porous Ni support sheet for the first time by use of a secondary growth method. It is found that uniform seed coating on the support is necessary to form a continuous membrane. In addition to growth time and temperature, presence of a modulator in the growth solution is found to be useful controlling parameters for hydrothermal membrane growth on the seeded support. A dense, inter-grown membrane layer is formed under 140 ^{o}C and 160 ^{o}C for 24 h with modulator addition. The membrane surface comprises 500 nm octahedral crystals, which are supposed to grow out of the original 100 nm spherical seeding crystals. The separation characteristics of resulting membranes are characterized with pure CO_2, air, CO_2/air mixture, and humid CO_2/air mixture. CO_2 permeance as high as 1.9E-06 mol/m^2/s/Pa at 31^{o}C is obtained. Unlike the hydrophilic zeolite membranes, CO_2 permeation through this membrane is not blocked by the presence of water vapor in the feed gas. The results suggest that this MOF framework is a promising membrane material worth to be further investigated for separation of CO_2 and other small molecules from humid gas mixtures.

55 The Latest Development of Thin-Sheed Zeolite Membranes for Building Applications

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Effects of Pyrolysis Conditions on Gas Separation Properties of 6FDA/Detda:Daba(3:2) Derived Carbon Molecular Sieve Membranes.

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A previously reported polyimide, 6FDA/DETDA:DABA(3:2), was pyrolyzed under different protocols to produce carbon molecular sieve (CMS) dense film membranes for separation of important gas pairs, including pure gases CO_2/CH_4, O_2/N_2 and mixture gases 50% CO_2/50% CH_4 and 50% C_3H_6/50% C_3H_8. This study investigated the effects of pyrolysis temperature, O_2 doping, and precrosslinking on the separation performance of 6FDA/DETDA:DABA(3:2) CMS membranes. Comparing to the precursor membranes, separation performance of all 6FDA/DETDA:DABA(3:2) CMS membranes improves significantly with both higher permeability and selectivity. The CMS film pyrolyzed with a novel method, i.e., 800 ^{o}C with precrosslinking, shows very attractive separation performance with CO_2 and O_2 permeability of 4678 Barrer and 683 Barrer, CO_2/CH_4, O_2/N_2 selectivity of 71.5 and 8.0. Sorption measurements provide insight into the pore size distributions among these CMS membranes. The effects of these three parameters during pyrolysis on the CMS membranes gas separation performance are summarized and compared, hypotheses regarding the structure changes brought about by changing these parameters are also provided.

High-Performance Zeolitic Imidazolate Framework ZIF-8 Membranes Fabricated By Interfacial Microfluidic Processing in Polymeric Hollow Fibers.

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High-performance ZIF-8 Membranes for Propylene Separation Fabricated by Interfacial Microfluidic Processing in Polymeric Hollow Fibers

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Metal Organic Frameworks (MOFs) are nanoporous materials consisting of organic linkers coordinated to metal ions in crystalline structure. They are potentially attractive as energy-efficient gas separation materials and membranes.[1] The MOF material ZIF-8 has great potential for use in C_3H_6/C_3H_8 separation membranes. However, industrial propylene separation relies on energy-intensive high-pressure distillation due to the lack of a high-performance membrane that can meet operating requirements.[2] Most of the reported ZIF membranes are fabricated by non-scalable techniques or develop defects when challenged at higher pressures (5-10 atm). Previously, we have reported a novel membrane fabrication technique called Interfacial Microfluidic Membrane Processing (IMMP) that has potential to overcome scalability and economic feasibility issues.[3]Here, we will discuss in detail the unprecedented high performance of ZIF-8 hollow fiber membranes achieved by rational engineering of the IMMP technique, to yield membranes with excellent selectivities and permeances at ambient conditions as well as elevated pressures and temperatures of industrial interest.

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Separation of Olefins and Paraffins Using Stable Customized Amorphous Fluoropolymer (CAF) Membranes.

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The oil and gas industry expends 250 trillion BTU/year separating olefins and paraffins (e.g., propylene from propane) through the use of costly and energy intensive distillation columns, a technology that is little changed in the last 40 years. The separations of these materials are some of the costliest, most energy intensive, and most technically difficult separations in the industry due to the very similar size and nature of the molecules being separated. The ability to separate these materials using a stable membrane would provide substantial economic benefit to petrochemical processes and dramatically decrease the energy required.

Using customized amorphous fluoropolymer (CAF), Compact Membrane Systems has developed membranes which have shown high propylene flux and propylene/propane selectivity over a period of greater than 180 days. The permeance and selectivity combination of the membranes are above the industry Robeson curve. While we have previously shown data for propylene/propane separation, we have recently demonstrated the ability to separate C2s (as well as C3s) obtaining very high olefin permeance (~270 GPU) and selectivity (>70) for ethylene/ethane separation. In addition, membrane stability was evaluated in presence of poisons such as hydrogen sulfide, acetylene and hydrogen. We will discuss these results as well as some of our economic modeling showing very low payback times and positive IRRs for a variety of scenarios governing petrochemical processes.

56 Organo-Soluble Polybenzoxazoles (PBOs) As Gas Separation Membranes: New Synthesis and Gas Transport Properties.

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N/A Membrane.

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Influence of Humidity on Sulfonyl-Containing Polybenzimidazoles for Gas Separations.

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Due to their high chemical and thermal stability, polybenzimidazoles (PBIs) are promising candidates for use as gas separation membranes for high temperature applications. A series of sulfonyl-containing PBIs based on the 3,3’,4,4’-tetraaminodiphenylsulfone (TADPS) monomer were recently synthesized and shown to have enhanced solubilities in common organic solvents relative to commercial PBI (Celazole^{TM}), thus improving their processability. Celazole^{TM} and TADPS-based PBIs show a strongly hydrophilic behavior, and can uptake up to 25% water by mass at room temperature. Due to the potential effects of water uptake on both mechanical and gas transport properties, this study seeks to understand the fundamentals of the interactions between water and PBIs. Water vapor gravimetric sorption and dilation measurements have been performed at 35 °C, and a significant hysteresis was observed during desorption experiments, due to swelling and plasticization. The specific volume of the water-polymer mixture as well as the partial molar volume of water in the glassy polymer have also been calculated. Furthermore, a separate FTIR analysis showed that strong hydrogen-bonding interactions occur between water molecules and the PBI backbone.

GAS SEPARATION II - CO2 SEPARATION

Crosslinked Polyimide Hollow Fiber Membranes for CO2 Removal from Natural Gas: From Laboratory to Field (Featured talk).

__Daniel Chinn__[1], Nitesh Bhuwania[1], Shabbir Husain[2], Stephen Miller[1], Claire Daniel[2], and Katherine Bell[2]
(1)Chevron, Richmond, CA, (2)Chevron, Houston, TX

Polymeric hollow fiber membranes can remove CO_2 from natural gas with compact modular systems that have a small footprint and low operating cost, making them especially attractive for offshore applications. While these membranes have demonstrated attractive performance in selectivity and productivity, the sensitivity of the polymer membrane to impurities and harsh conditions continues to be a drawback. These impurities, such as C_3+ hydrocarbons, as well as a high partial pressure of CO_2, due to its enhanced solubility in glassy polymers, can lead to swelling (plasticization) of the polymer, resulting in a loss of selectivity. This has led to considerable research in polyimides containing crosslinkable groups within the chains which, upon crosslinking, have shown significantly more resilience to degradation by impurities or high CO_2 pressure. Such crosslinkable groups include carboxylic acids which can then form chemically crosslinked bonds with multifunctional alcohols. Chevron's proprietary XLP (Cross-Linked Polyimide) hollow fiber membrane technology, developed in a joint program with Georgia Tech, offers both high flux and high selectivity, and attractive robustness for CO_2/CH_4 separation. This presentation will cover these aspects of XLP membranes:

1. The evolution of XLP membranes from university R&D to industrial bench-scale
2. How advanced gas-separation membranes, such as XLP create value from an end-user perspective
3. Performance testing of XLP membranes, from clean laboratory environments to harsh field conditions
4. Commercialization aspects of XLP and areas for further performance optimization

57 Pilot-Scale Development of a PEEK Hollow Fiber Membrane Contactor Process for Post-Combustion CO2 Capture.

__Shiguang Li__[1], Travis Pyrzynski[1], Naomi Klinghoffer[1], Timothy Tamale[1], James Aderhold[1], S. James Zhou[1], Howard S. Meyer[1], Yong Ding[2], and Benjamin Bikson[2]

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58 High Ionic Liquid Content Membranes for Effective Biogas (CO2/CH4) Separation.

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High Performance UV-Irradiated PIM-1-Based Mixed-Matrix Membranes for Carbon Capture.

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A series of mixed-matrix membranes (MMMs) consisting of zeolitic imidazolate framework-71 (ZIF-71, $Zn(dcIm)_2$) and polymer of intrinsic microporosity (PIM-1) were investigated before and after ultraviolet (UV) irradiation for various gas separations. Well compatible MMMs are formed between ZIF-71 nanoparticles and PIM-1. The incorporation of ZIF-71 considerably enhances the gas permeability without compensating the gas pair selectivities of O_2/N_2, CO_2/N_2 and CO_2/CH_4. The PIM-1 comprising 30 wt% ZIF-71 exhibits a 154% increase in CO_2 permeability. FESEM and PAS confirm the formation of an ultrathin dense layer at the membrane surface after the UV treatment. The UV-irradiated PIM-1 has CO_2/CH_4, CO_2/N_2 and O_2/N_2 selectivities of 34.1, 29.8 and 6.7, respectively. The UV-treated MMMs possess much higher permeability compared to that of pristine UV-irradiated PIM-1 with similar gas pair selectivities. Under mixed gas tests, the UV treated PIM-1 containing 20 wt% ZIF-71 has a CO_2 permeability of around 2000 barrers and a CO_2/CH_4 selectivity of 32. This performance outperforms PIM-1 and UV treated PIM membranes. The UV-PIM-1/ZIF-71 membranes have superior separation performance with both high permeability and selectivity for CO_2/CH_4 or other gas pair separation.

CO2 Capture from Power Plant Flue Gas By Polaris Membranes: Update on Field Demonstration Tests.

Jay Kniep[1], *Carlos Casillas*[1], *Ken Chan*[2], *Don Fulton*[1], *Jurgen Kaschemekat*[2], *Jennifer Ly*[2], *Tim Merkel*[3], *Vincent Nguyen*[3], *Zhen Sun*[1], *Xuezhen Wang*[1], *Xiaotong Wei*[3], *and L. S.*

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Working with the US Department of Energy, MTR has developed new membranes and process designs to recover CO_2 from power plant flue gas. MTR Polaris membranes have CO_2 permeances ten times higher than standard commercial membranes, which greatly reduces the cost of a membrane capture system. These membranes are combined with a novel process design that uses incoming combustion air to sweep membranes and recycle CO_2 to the boiler. Design calculations estimate that this membrane process can capture 90% of the CO_2 in flue gas as a supercritical fluid using approximately 25% of the plant power, at a cost of $40-$50/ton of CO_2 captured. This translates to an increase in the levelized cost of electricity of about 50%.

In 2010, MTR completed a three-month field demonstration of the membrane CO_2 capture process with Arizona Public Service (APS) at their Cholla coal-fired power plant. The pilot system used commercial-scale membrane modules, and removed 90% CO_2 from a post-FGD flue gas slipstream containing 1 ton CO_2/day. In late 2011, the system was moved to National Carbon Capture Center (NCCC) operated by Southern Company in Birmingham, AL, for further demonstration. Overall, the system has an accumulated run time of over 10,000 hours, and the membrane modules have exhibited stable performance. With experience learned from these tests, MTR has designed a scale-up small pilot unit to capture 20 ton CO_2/day from a power plant slipstream (equivalent to 1 MW_e-scale power generation). The system was initially commissioned in August 2014 and testing concluded in June 2015. During testing, advanced modules demonstrating higher packing density, lower pressure drop, and cost savings were validated. Current work involves fully integrating the small pilot unit with Babcock & Wilcox's (B&W) 1.8 MW_{th} coal fired research boiler in Barberton, OH. The field demonstration to be conducted at B&W will be the first time membrane operation with real flue gas and boiler operation with CO_2-laden air have been conducted in a single test. Technical results to date for the field tests, and future plans on technical development will be discussed in this presentation.

Bench Scale Testing of Next Generation Hollow Fiber Membrane Modules.

***David Hasse**[1], Alex Augustine[2], Sudhir Kulkarni[3], Trapti Chaubey[2], Dean Kratzer[1], Shilu Fu[4], and Edgar S. Sanders[5]*
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Air Liquide (AL) is developing a next generation polyimide membrane material (PI-2) for application in our cold membrane hybrid process for CO_2 capture. Combining the cold membrane operation with an integrated CO_2 compression and purification unit significantly reduces the overall cost of CO_2 capture. The current work is aimed at developing the PI-2 material to a commercial scale, then validating its performance under real flue gas conditions.

Previous work (including grants DE-FE0004278 and DE-FE0013163) showed promising results for the cold membrane hybrid process utilizing the commercial available AL membrane bundles (PI-1 material). The Levelized Cost of Electricity (LCOE) for 90% CO_2 capture from a 550 MWe net coal power plant was projected to increase by 48 – 53%. The cold membrane technology was demonstrated at the National Carbon Capture Center with a 0.3 MWe field-test unit incorporating two 12” OD PI-1 commercial membrane bundles. That system exceeded its performance targets with stable membrane operation for over 500 hours. Finally, the new PI-2 membrane fiber was spun at lab scale and showed significant performance improvements: up to 10 times the CO_2 permeance and similar CO_2/N_2 selectivity as the existing commercial fiber (3 – 5 times the potential productivity per bundle).

The current project seeks to develop this next generation PI-2 material to a technology readiness level of 5 via manufacturing scale-up and testing with 300 - 1,000 Nm^3/h of real flue gas, 0.1 - 0.3 MWe equivalents. Air Liquide manufacturing methodology will be applied to fabricate prototype membrane modules. Once the manufacturing methods prove reliable and performance is demonstrated in line with expectation, commercial scale bundles will be fabricated. Those commercial scale bundles will be performance tested with real flue gas at the National Carbon Capture Center. Finally, simulation studies of novel hybrid processes have begun that take advantage of the next generation fiber performance. The advantages and drawbacks of several arrangements will be discussed.

The current development work is supported by the Department of Energy National Energy Technology Laboratory under Award Number DE-FE0026422 (J. Figueroa, Program Manager).

60 Dual CO2- and N2- Selective Intrinsically Microporous Hydroxyl-Functionalized Triptycene-Based Polyimide for Natural Gas Upgrading.

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GAS SEPARATION III - NEW CONCEPTS

Physical Aging of Perfluoropolymers in Ultrathin Film Composite Membranes and Its Interpretation Using the Free Volume Model.

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Thin film composite (TFC) membranes for gas separation are comprised of a selective layer of glass polymers, which are usually subjected to physical aging, i.e. permeability decreases with time. The aging behavior has been ascribed to the rearrangement of polymer chains in the thin film, resulting in changes in free volume (f) and glass transition temperature (T_g). Our objective is to investigate the effect of physical aging on gas permeance, selectivity and T_g of the selective layer in the TFC membranes. Two-layer TFC membranes consisting of perfluoropolymers of Teflon® AF or Hyflon® AD at various film thicknesses (50 – 400 nm) on polyethersulfone ultrafiltration support were prepared. Pure-gas permeances of CH_4, N_2, H_2 and CO_2 at 35 °C were measured and monitored for aging over 1000 hr. Apparent T_g of the thin selective layer was measured over time by a new thermo-mechanical method, Nano Thermal Analysis. In general, aging decreases gas permeances and increases T_g, and the rate of changes is more significant for thinner films. For example, after aging for 2000 hr, N_2 permeance decreases from 1000 gpu to 550 gpu by 45% and T_g increases from 160 °C to 172 °C in a TFC membrane with 100-nm thick Teflon® AF1600. In this talk, we will compare the aging behavior and gas permeance reduction of the TFC membranes with those of freestanding thin films. More importantly, for the first time we have developed a correlation between the gas permeance reduction and T_g increase using the free volume model to explain the physical aging behavior.

61 New Membrane Based Hybrid Unit Operation for Gas Separation.

Ferruccio Doghieri[1]*, Matteo Minelli*[1]*, Giulio Sarti*[2]*, Francesco Miccio*[3]*, Valentina Medri*[3]*, and Elena Landi*[3]
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62 Steric Hindrance Effect Demonstrated in Polyvinylamine Facilitated Transport Membranes for CO_2 Separation.

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Reverse Selective Glassy Polymers for Higher Hydrocarbon Removal from Natural Gas.

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Saudi Arabia owns one of the largest proven reserves of natural gas in the world. Much of this resource is utilized for domestic energy production; however, other opportunities exist for natural gas monetization, such as fuel gas conditioning and recovery of C_3^+ hydrocarbons for feedstock and petrochemical applications. As such, Saudi Aramco has strong interest in developing gas separation membranes for improving the recovery of C_3^+ hydrocarbons from methane in existing liquid recovery units (LRU). In this case, reverse selective membranes are needed in order to retain methane on the high pressure so that recompression into transmission pipelines can be avoided. Recently, a series of novel glassy polynorbornenes was developed that demonstrates improvement in mixed gas C_3^+/C_1 selectivity relative to commercial PDMS under field relevant conditions. Through a systematic study in the transport properties of these materials under industrially-relevant feed streams, the effect of polymer structure as well as crosslinking on membrane performance has been elucidated. This talk will discuss mixed gas transport results of these polynorbornenes compared to commercial PDMS, demonstrating the promise of these glassy membranes for reverse selective membrane applications.

64 Transferring Membrane Polymer Properties into Gas Separation Process Performance.

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Pressure-Vacuum Swing Permeation: A Novel Process for Gas Separations.

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A novel process mode for gas separation by means of membranes was presented. It involved cyclic pressure-vacuum swings for feed pressurization and permeate evacuation, thereby increasing the transmembrane pressure difference and the feed to permeate pressure ratio. The feed pressurization and permeate evacuation were preferably accomplished using a single pump capable of pressurization and suction. Unlike transient permeation processes reported in the literature which were based on the differences in sorption uptake rates or desorption falloff rates, this process was based on the selective permeability of the membrane for separations. The dynamic gas permeation process associated with the pressure-vacuum swing permeation was analyzed to elucidate the working principle of the process, and a parametric study was carried out to evaluate the effects of design and operating parameters on the separation performance. To exemplify the feasibility and effectiveness of the process, air separation for oxygen enrichment and CO2 separation from lanfill gas were investigated as representative applications. It was shown that the separation efficiency was enhanced by means of the pressure-vacuum swing, and both product purity and product throughput higher than those from conventional steady-state permeation could be obtained.

MEMBRANE REACTORS AND CONTACTORS

Polymeric, Catalytic, Conductive, Porous Hollow Fiber Membrane Cathode for Water and Energy Recovery from Wastewater Treatment.

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Polymeric porous hollow fiber membrane (HFM) is regarded as revolutionary solution in the wastewater industry for recovery of clean water at low cost. Further advancing research towards the energy recovery using microbial electrochemical principle has been conceptualized by precisely modifying polymeric porous HFMs to become catalytic and electrically conductive. The polymeric catalytic conductive HFMs were used as a cathode in anaerobic electrochemical membrane bioreactor (AnEMBR) for recovery of both water/energy from low organic strength wastewaters (such as sewage). In turn this mechanism also reduces biofouling by membrane scouring through the generation of H_2 bubbles on the surface of the membrane and/or generation of electrical field. The advantage of such membranes in biological waste water treatment has been reported for polymeric flat sheet [1] and inorganic HFM [2].

In this study, we have investigated the development of multilayer polymeric catalytic and conductive porous HFM cathodes using atomic layer deposition (ALD) technique. These fibers were compared with the benchmark Pt-coated (0.5 mg Pt/cm^2) carbon cloth cathodes (control reactor) generally used in microbial electrochemical systems research. They were used as cathode in AnEMBR and operated in electrolysis mode under applied potential (-0.1V vs Ag/AgCl). The e^- and H^+ generated at the anode ultimately get reduced to H_2 on the surface of cell cathode. The performance of the AnEMBR in terms of fouling propensity was compared with a control reactor, which was operated as an anaerobic MBR (AnMBR). The AnEMBr fouled significantly less than that of AnMBR due to the indigenous H_2 evolution on the conductive fibers surface. Their dual functionality and architecture open the window for sustainable harnessing of resources from wastewaters (i.e. pollution to purification) and mitigating the unavoidable phenomenon of biofouling in membrane processes.

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High-Temperature Membrane Reactors: An Effective Approach for Equilibrium-Limited Reactions.

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Reaction and separation are considered as two of the most crucial steps in chemical plants. Performance of each of these two steps can strongly affect the profitability of a given process by affecting its raw materials and energy demand and consumption. In an effort to improve the overall performance of the process, reaction and separation can be combined into a multifunctional Membrane Reactor (MR) that offers a platform for simultaneously carrying out the reaction and separation steps in one single stage. Such reactors typically consist of a catalyst bed in contact with a high-temperature membrane that either enables the removal in situ of one or more products (extractive MR) from the system or the controlled dosing of one or more of the reactants (contactor MR). Replacing the conventional two-stage reaction and separation systems with such a multifunctional reactor increases the process synergy, reduces the by-product formation as well as amount of reactants consumed. Additionally, a considerable reduction in the overall energy costs is to be expected [Sanchez and Tsotsis, 2002; Soltani et al., 2013]. While there are several reports on the applications of MR for both gas and liquid phase reactions, further studies are still required to characterize and optimize their performance, and to move towards commercialization of these multifunctional reactors [Sanchez and Tsotsis, 2002; Soltani et al., 2013].

In this talk, we will present two different examples of high-temperature MR currently under investigation by our Group. The first is a extractive MR that is used for methanol (MeOH) synthesis, and the other a contactor MR that is used for carbon (CO_2) capture and utilization (CCU). Synthesis of MeOH from syngas is a severely equilibrium-limited reaction, which means that a large fraction of the unreacted syngas feed, must be recycled to make this equilibrium-limited process economically feasible. The ability of MR to increase the per-pass yield makes them a optimal choice for process intensification [Soltani et al., 2013], particulalry for coal-deruved and biomass-derived syngas from air-blown gasifiers that contains considerable amounts of inert N_2.

Power plants are responsible for a large fraction of the man-made carbon-dioxide emissions, and are major contributors to the green house effect. Thus, reducing the amount of CO_2 emissions from such plants is of the utmost importance. The key challenge here is the dilute CO_2 concentration in the flue-gas, which make the conventional approaches such as direct sequentration technically as well as economically inefficient. Coupling of reaction and separation in a contactor MR, provides the driving force for the separation which moderates the challenge of separating dilute CO_2 from flue-gas, and can also produce valuable products (e.g., synthetic natural gas, alcohols, etc.) which can be used as fuels to reduce the overall energy demand of the plant, and to improve its efficiency.

During our talk, we will present the two multifunctional reactor configurations that are being presently experimentally investigated, and will discuss the influence of reaction conditions and separation efficiency on the final yield of the reaction. The different types of high-temperature membranes that have been investigated will be described, and the influence of membrane characteristcs on overall system performance will be described. Efforts to optimize MR performance both experimentally and numerically will be furher outlined.

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67 **Bio-Mimetic Hollow Fiber Membrane Contactor Process for Low-Cost High-Purity Oxygen Production.**

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Influence of Microporous Membrane Properties on VMD and DCMD.

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A variety of microporous hydrophobic flat sheet membranes of polyvinylidene fluoride (PVDF) and expanded-polytetrafluoroethylene (e-PTFE) were studied to evaluate the influence of membrane properties on their performance in desalination by vacuum membrane distillation (VMD) and direct contact membrane distillation (DCMD) processes. The membrane thickness was varied between 23 µm to 125 µm; the pore size was varied from 0.05 µm to 0.45 µm. The porosity was generally high in the range of 0.7-0.8. VMD experiments were performed over a hot brine temperature range of 65 °C to 85 °C for various feed flow rates and various vacuum levels in a rectangular chlorinated polyvinyl chloride (CPVC) cell. Membrane properties, such as the maximum pore size, tortuosity as well as the liquid entry pressure (LEP) were experimentally determined. Water vapor fluxes were predicted and compared using two models: the Knudsen diffusion and the dusty-gas model (DGM). The deviation between two models is within 1.3 %. Knudsen diffusion is the dominant regime in VMD transport since Knudsen number, K_n, for all membrane were larger than 1 at all temperatures. The boundary layer heat transfer resistance in the membrane cell and the membrane surface temperature were determined from experimental data via Wilson plot. Good agreements of membrane mass transfer coefficients and water vapor fluxes were found between the DGM simulations and the experimental results (deviation within 5%). Same membranes were studied in a circular stainless steel cell and the CPVC cell for DCMD behavior using the Wilson plot method. Experimental and predicted values of the membrane mass transfer coefficients and water vapor fluxes have been compared for brine temperature range of 65°C - 85°C and distillate temperature at 25°C. Pore size distribution (PSD) did not matter if the membrane pore size variation falls entirely in the Knudsen diffusion or the transition regime. However, for membranes having nominal pore size □ 0.1 µm, K_n □ 1, PSD played an important role in DCMD. The effect of membrane thickness on water vapor flux and thermal efficiency were also simulated and compared with the experimental results.

68 **Development of Multibore Hollow Fiber Membranes for Water Deoxygenation.**

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69 **Fabrication & Performance Study of Pd-Au PSS Supported Membrane Reactor Via Natural Gas Steam Reforming.**

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MEMBRANE TRANSPORT: THEORY AND CHARACTERIZATION TOOLS

Transport of Organic Compounds in DCMD.

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New Insights into Salt Transport Mechanism in Membrane Desalination.

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New Insights into Salt Transport Mechanism in Membrane Desalination

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Despite >50 years of industrial membrane desalination, salt transport in membranes (NF and RO) and membrane structure are still insufficiently understood. Our group has studied the mechanism of membrane transport using two basic methods: theoretical

analysis using analytical models and molecular dynamics and experimental measurements using filtration data and impedances spectroscopy of genuine and model membrane films. Some open fundamental questions we tried to address were:

1) Why polyamide has been the best material for RO/NF membranes

2) What is the actual bottleneck of salt transport in RO/NF: a nanopore or a dense film?

3) What is the charge of the membrane and how does it uptake salt?

4) How much salt uptake and salt transport are related;

5) How much role ion-specific effects (including H^+ and OH^-) play in salt sorption and transport;

6) How separation of complex ion mixtures (including pH changes) should be modelled etc.

Even though some question still remain open, we seem to have obtained (partly surprising) answers to some of the above questions, which will be presented in the talk.

Numerical Simulations of Concentration Polarization and Mineral Scaling in Reverse Osmosis Systems.

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Fluid flow and mass transport in reverse osmosis (RO) systems are difficult to simulate numerically due to the coupling between the transmembrane filtrate flow, pressure, and osmotic pressure. This coupling is particularly challenging for real-world systems in which the local filtrate flow varies both spatially and temporally, and is further complicated for systems in which filtrate flow is also affected by mineral scaling and membrane fouling. Consequently, previous simulations of RO tend to focus on two dimensional steady cases. We present a numerical method specifically tailored to simulating RO. Using the method, we simulate the transient formation of concentration polarization layers as a function of feed Reynolds number, solute concentration, and transmembrane pressure. From the computed flow fields, we investigate the importance of advection and diffusion of solutes both normal and tangential to the membrane surface. Contrary to the thin-film approximation, we find that normal diffusion can be balanced by both normal and tangential advection within the concentration polarization layer. Finally, we use our method to simulate the transient decline in filtrate flux due to the precipitation of sparingly soluble salts on the membrane surface.

Membrane Porous Structure and Its Impact on Permeability and Selectivity.

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Membranes comprise complex porous structures, either as the actual separation medium, e.g. in the case of Dialysis, Micro- and Ultrafiltration or, in the case of composites used for gas separation, Nanofiltration and Reverse Osmosis, where an underlying porous support can impact the overall performance of the membrane. Such structural features have a wide impact on membrane performance, ultimately dictating the water permeability and solute selectivity as well as concentration polarization, propensity for and severity of fouling.

The porous structures can be characterized by their pore-size distribution as well as their spatial distribution, which can further be divided between the membrane surface distribution vs the depth distribution. Here, we theoretically probe the relative importance of these distributions for several illustrative cases: pressure-driven flow as impacted by membrane surface pore locations and depth morphologies, the obstruction presented by a support layer to diffusion through the overlying thin-film, and the selectivity of a porous membrane as affected by a porosity gradient. In particular, we examine the difference between periodic and random spatial distributions of pores.

Separation membranes come in many morphological forms, mostly dependent on the materials used as well as the fabrication method and conditions. Identifying advantageous porous structures would benefit design and motivate the development of better control over the formation of a given morphology.

71 Twisted Hollow Fiber Membranes for Enhanced Mass Transfer.

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72 How Do Hydrodynamic Conditions in Spiral Wound Membrane Elements Translate into Shear Forces Effective for Fouling Control at Membrane Surface?.

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Prediction of Vapor Recovery from Light Gas with Mesoporous Membranes Using Dynamic Mean Field Theory.

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Mesoporous membranes have great potential for the separation of condensable species such as in the recovery of volatile organic compounds from air or the removal of carbon dioxide from flue gas. Selectivity and permeance of membranes in these processes are influenced by mechanisms like preferential adsorption, surface flow, and capillary condensation, but predictive correlations relating these mechanisms to mesopore properties such as geometry and surface chemistry are absent. Atomistic simulations provide a pathway to such correlations but are computationally intensive. Dynamic mean field theory (DMFT), a lattice-based density functional theory that successfully describes adsorption equilibrium and uptake dynamics in mesoporous materials, is a less intensive approach that provides qualitative and semi-quantitative insight. We have recently adapted DMFT to study non-equilibrium steady-state transport in mesopores and published a computational analysis of a permporometry experiment, in which a light gas permeates through a membrane in the presence of an essentially static condensable vapor. In this work, we use DMFT to study the recovery of a condensable vapor from a light gas, a situation in which the vapor is under a substantial partial pressure gradient. Model parameters are chosen to be relevant to experimental work in the literature on recovery of volatile organic compounds (VOCs) from air. Even in a simple slit pore, the results show interesting new phenomena like capillary condensation that is confined to the part of the pore closest to high pressure (feed side) of the membrane. We explore how modifying the geometry of the pore influences the selectivity and permeance, which will be useful to researchers designing mesoporous membrane materials to perform such separations.

MEMBRANES FOR BIO-SEPARATIONS AND DEVICES

Purification of Oncolytic Viruses - a New Challenge for Membrane Processes.

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Oncolytic viruses (OVs) are a class of cancer therapies that are currently going through clinical trials on their way to full approval. They are attractive given their inherent specificity for disease targets. The upstream production procedure of these bio-therapeutic molecules vectors results in a high amount of cell debris, host cell proteins, and nucleic acids that must be removed to meet the guidelines of regulatory authorities. Thus, there is a need for robust, high-yielding manufacturing downstream processes (DSP) to improve the speed of production, along with the yields and purity of OV products. One of the primary challenges during production is the final sterile filtration step – some recent studies have reported an over 80% loss in the vector titer. The objective of this study is to develop new filtration processes that can achieve the required purity requirements but at the higher throughputs and lower losses that are needed for full-scale production of OVs.

For this work, a purified lot of the Maraba virus (MG1) was provided by the Mulcahy Family Manufacturing Facility (at the Ottawa Hospital Research Institute) to study the filtration performance in a dead-end (i.e. normal flow) configuration. The Maraba virus is from the rhabdovirus family and features a unique bullet-shaped, enveloped structure. The effects of formulation buffer conditions (salt concentrations, buffer type, buffer concentrations, and pH values), membrane type, and the length of the holding time before the filtration step were studied. Our hypothesis is that virus aggregation is the dominant reason for the high losses reported in recent studies. The transmembrane pressure (TMP) profile was used to monitor for membrane fouling and the number of plaque forming units (PFUs) was used to assess the virus concentration. Future work will use unpurified lots of the same Maraba virus solution to assess the performance of different membrane filters under actual DSP conditions.

Voltage Activated Membrane Platforms for Drug Delivery and Bioseparation.

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Voltage Activated Membrane Platforms for Drug Delivery and Bioseparation

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An important challenge for the membrane community is to mimic the dynamic activity of natural protein channels that outperform by orders of magnitude man-made systems based on pore size and coarse chemical selectivity. To mimic protein channel pumping on a robust engineering membrane platforms applied bias can be used to actuate charged gatekeepers and induce ionic pumping. Described here are two platforms of Carbon nanotube membranes and Anodized Aluminum Oxide (AAO) with nm-thick electrodes at pore entrances/exits. Carbon nanotubes have three key attributes that make them of great interest for novel membrane applications 1) atomically flat graphite surface allows for ideal fluid slip boundary conditions and extremely fast flow rates [***1,2***] 2) the cutting process to open CNTs inherently places functional chemistry at CNT core entrance for chemical selectivity and 3) CNT are electrically conductive allowing for electrochemical reactions and application of electric fields gradients at CNT tips. The CNT membrane, with tips functionalized with charged molecules, is a nearly ideal platform to induce electro-osmotic flow with high charge density at pore entrance and a nearly frictionless surface for the propagation of plug flow. Through diazonium electrochemical modification we have successfully bound anionic surface charge to CNT tips and along CNT cores. High electro-osmotic flows of 3 cm/s-V at are seen that are 10,000 fold faster than in conventional nanoporous materials[***3,4***] and are consistent with pressure driven flow enhancements. Use of the electro-osmotic phenomenon for responsive/programmed transdermal drug delivery devices for nicotine addiction [***5***]. Another approach is to mimic natural protein channel transport cycles with binding/transport/release/reset events. Porous alumina (AAO) membranes have top and bottom electrodes coated with thin Au layers with pore dimension tuned to match protein dimensions. At this thin layer at pore entrances, Ni-ETA is able to bind to hys-tag residue on target protein, as is commonly employed in chromatography. A binding voltage pulse attracts anionic target protein to top electrode and blocking the pore, while repelling the cationic imidazole release agent. The second voltage cycle attracts cationic release agent to top of membrane while pumping anionic target protein to bottom permeate and resetting the pumping cycle. This system was able to successfully mimic natural membrane transporter cycles and the separation efficiency of 1cm2 of membrane was comparable to convention 1cm3 volumes used in chromatography [***6***]

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Developing High Performance Responsive HIC Membrane Adsorbers.

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Fast convective mass transport, low pressure drop and better accessibility to large biomolecules make membrane adsorbers an attractive alternative to packed-bed chromatography used in the downstream process. Responsive hydrophobic interaction chromatography (HIC) membranes are investigated for protein purification in a bind/elute mode. The surface of these responsive HIC is grafted with polymeric ligands with tunable hydrophobicity. Unlike traditional HIC ligands, responsive HIC ligands can switch between hydrophobic state (under high salt) and hydrophilic state (under low salt) for protein binding and elution respectively reducing the possibility of irreversible binding.

Thermo-responsive poly (N-vinyl caprolactam) (PVCL) ligands have been grafted on the surface of regenerated cellulose membrane (0.45 µm pore size) via atom transfer radical polymerization (ATRP). The conformations and degrees of hydration/dehydration of these responsive ligands are concentration and salt specific. Systematic studies have been performed to understand and optimize the chromatographic behavior of these responsive HIC membranes using BSA and IgG as model proteins. In addition, the effects of copolymerization with other monomers such as hydroxyethyl methacrylate, N-(2-hydroxypropyl) methacrylamide and hydroxyethyl acrylamide on binding capacity and recovery were also investigated. Our results suggest that the 3-D conformation, monomer property and composition all strongly affect the binding capacity and recovery.

73 Rapid Uranium Isotopic Analysis Using Ultrafiltration and Alpha Spectroscopy.

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74 A Method to Evaluate Membrane Protein Compatibility with Biomimetic Membranes.

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75 **Fabrication of Ultrathin ZnO Nanocrystal-Nanocellulose Composite Paper.**

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Concentrating Membrane Proteins without Concentrating Detergent.

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MICRO, ULTRA, AND NANO-FILTRATION APPLICATIONS II

77 **Comparison of Polymeric and Ceramic MF/UF Membranes for the Treatment of Produced Water.**

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79 **Desalination of Brackish Inland Surface Water Using Nanofiltration: Fouling Control and Water Quality Improvements.**

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80 **Influence of Chemical Coating Combined with Nanopatterning on Alginate Fouling during Nanofiltration.**

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81 The Impact of Slickwater Fracturing Fluid Composition / Fracturing Interactions on Membrane Fouling of Flowback Water.

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82 Removal of Human Adenovirus 40 in Membrane Bioreactors: Roles of Membrane Pore Size, Fouling, Pressure Relaxation and Membrane Cleaning.

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Filtration of Fine Particles in Atmospheric Aerosol with Electrospinning Nanofibers.

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In this study, a needleless electrospinning was studied, and the equipment was set up through theoretical simulation and a large number of experiments. The polylactic acid (PLA) nanofibers were prepared for filtering the aerosols by electrospinning. The PLA nanofibers mats were used as the middle layer to design the composite filter membranes. The atmospheric aerosols were used as dust sources in filtration test. The results showed that the filtration efficiency of the composite filter media was increased along with the thickness of nanofibers mats which was controlled by the collection time during the electrospinning. The filtration efficiency can be improved obviously by compositing with a thin layer of nanofibers. Moreover, the size distributions of atmospheric aerosols were monitored by the scanning mobility particle sizer spectrometer and the optical particle sizer. The size of particles in atmospheric aerosols was primarily distributed in range of less than 1 μm. It showed different changes with the mass concentrations of PM 2.5 (particulates with an aerodynamic diameter of ≤ 2.5 μm) for different sizes of fine

particles. The amount of fine particles (less than about 60 nm) was decreased while the larger ones (> 60 nm) increasing along with the mass concentrations of PM 2.5 in atmospheric aerosols. That was due to the formation of the secondary atmospheric aerosols.

Removing Mercury (II) from Wastewater By Polymer-Enhanced Ultrafiltration.

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Mercury (II) is one of the most strictly regulated contaminants released from various anthropogenic emission sources to the aquatic environment. When transformed to an organic form of methylmercury, it will be the most toxic, persistent and bioaccumulative form of mercury in nature. This study deals with removal of mercury (II) from wastewater by polymer-enhanced ultrafiltration (PEUF) using polyvinylamine as the mercury-binding polymer. A mercury removal rate as high as 99% was obtained, which was otherwise impossible to achieve with conventional ultrafiltration. Over the feed mercury concentration range tested (0 - 50 ppm), the PVAm dosage used did not affect the mercury rejection significantly, while water flux was reduced at a higher dosage of PVAm. A flux vs pressure relationship typical of ultrafiltration of macromolecular solutes was observed because of the presence of the amine polymer in the system, and the limiting flux appeared to follow the gel layer formation model. The fouled membrane surface was cleaned periodically with dilute chloric acid to recover the membrane permeability. Mercury removal with the PEUF was also tested with a simulated chlor-alkali wastewater that contained mercury and other chemicals (i.e., sodium chloride and sulphate), and the accompanying compounds in the feed solution was shown to influence the performance of PEUF for mercury removal.

Comparative Study of NF-RO Membranes for Sustainable Desalination of Produced Water and Frac Flowback Wastewater Following Biological Pretreatment.

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Development of unconventional oil and gas (O&G) resources is reshaping the energy landscape of the United States. Technological advances in hydraulic fracturing and horizontal drilling have made previously unrecoverable resources economically viable. However, extraction from these formations requires hundreds of thousands of gallons of clean water per well and generates substantial (and unavoidable) volumes of wastewater. These wastewaters (e.g., hydraulic fracturing flowback and produced water (PW)) contain varying concentrations of total dissolved solids (TDS), ranging from 10,000 mg/L to more than 200,000 mg/L, oil, grease, hydrocarbons, and various organic and inorganic matter. Consequently, a multi-barrier approach is required to effectively treat O&G waste streams for beneficial reuse.

Biological and membrane processes are promising methods to treat O&G wastewaters. Biological technologies have proven effective at removing organic material from a variety of waste streams including domestic waste streams, landfill leachate, and oily wastewaters; tight/dense membranes are most established in desalination of seawater and brackish waters. For sustainable membrane treatment, optimizing water recovery, and reducing fouling propensity, pretreatment targeting removal of organic constituents and suspended solids is critical. Integration of biologically-active filtration (BAF), ultrafiltration (UF), and nanofiltration/reverse osmosis (NF/RO) results in comprehensive removal and degradation of contaminants, reducing membrane fouling propensity due to BAF pretreatment, and producing a high quality permeate suitable for reuse applications such as hydraulic fracturing fluid and irrigation.

The current study evaluates the performance of NF/RO membranes following BAF and UF pretreatment of Denver-Julesburg (DJ) basin PW and frac flowback wastewater. The main objectives include (a) optimizing BAF and UF pretreatment for maximum removal of organic compounds, (b) evaluating NF/RO fouling propensity and membrane performance based on solids, inorganic, and organic rejection, and water flux, and (c) identifying favorable NF/RO membranes for treatment of PW and flowback, based on membrane characterization and performance. Bench-scale experiments with BAF have been conducted to acclimate a biofilm and optimize degradation of organic matter. In addition, experiments with UF were conducted to further reduce the turbidity of the BAF effluent and prepare it for NF/RO desalination. Ongoing NF/RO experiments compare the performance of various membranes (e.g., NF90, NF270, BW30 (DOW Chemical Company, Midland, MI), and NFX (Synder Filtration, Vacaville, CA)). Following rejection tests, membrane properties for each NF/RO membrane are being investigated using scanning electron microscopy (SEM) and atomic force microscopy (AFM) (morphology), contact angle (hydrophobicity), zeta potential (surface charge), and Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) (surface chemistry) to evaluate variations in fouling.

MICRO, ULTRA, AND NANO-FILTRATION APPLICATIONS I

85 Fouling and Scaling Behavior of Charged Nanofiltration Membranes and the Influence of Graphene Quantum Dot Surface Modification.

Andrew Colburn[1], *Namal Wanninayake*[2], *Doo Young Kim*[2], *and Dibakar Bhattacharyya*[1]
(1)Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY, (2)Department of Chemistry, University of Kentucky, Lexington, KY

Kam Agarwal
Patheon Inc, Mississauga, ON, Canada

86 Real-Time Fouling Monitoring and Characterization for Effective Operational Control of Ultrafiltration As Pretreatment for Sewater Desalination.

Han Gu[1]*, Larry Gao*[2]*, Anditya Rahardianto*[3]*, Panagiotis D. Christofides*[4]*, and Yoram Cohen*[3]
(1)Chemical & Biomolecular Engineering, University of California, Los Angeles, Los Angeles, CA, (2)Chemical & Biomolecular Engineering, UCLA, Los Angeles, CA, (3)Chemical and Biomolecular Engineering, University of California, Los Angeles, Los Angeles, CA, (4)Department of Chemical and Biomolecular Engineering and Department of Electrical Engineering, University of California, Los Angeles, Los Angeles, CA

88 Application of Ceramic Membranes in Treatment of Oil Sands Produced Water.

Saviz Mortazavi[1]*, André Yves Tremblay*[2]*, Yves Thibault*[1]*, Charbel Atallah*[2]*, Matthew Hudder*[1]*, Alex Doiron*[1]*, Joanne Gamage McEvoy*[1]*, and Derek Smith*[1]
(1)CanmetMINING, Natural Resources Canada, Ottawa, ON, Canada, (2)Department of Chemical and Biological Engineering, University of Ottawa, Ottawa, ON, Canada

Treatment of Surface Water By a Hybrid Coagulation and Immersed Ultrafiltration Membrane for Potable Water Production.

Esper Jacob Ncube
Process Technology, Rand Water, Johannesburg, South Africa

In recent years, surface water purification with ultrafiltration membrane has become an attractive alternative to conventional treatment. Some of the advantages of ultrafiltration membrane compared to conventional water treatment process include none or less use of chemical agents, good quality of produced water independent of feed water quality, good removal efficiency towards microorganisms, less production of sludge, compact process, and easy automation. Originally, ultrafiltration was used to remove turbidity and microorganism from good-quality surface water. Presently the main goal of this technology is for the removal of microorganisms, natural organic matter (NOM), dissolved organic matter (DOC) and other components. This trend can be attributed to the improved cost effectiveness of membrane systems as compared to conventional treatment

technologies such as filtration and to progressively more stringent water quality regulations.

This study examined the effect of hybrid process coagulation and ultrafiltration membrane performance for potable water production. An ultrafiltration system with a capacity of $24m^3/d$ was constructed to treat raw water taken from the impounded source water supplying the largest water utility in South Africa. A polyvinylidene (PVDF) hollow fibre ultrafiltration membrane was immersed in the process tank as the main component in the filtration system. The membrane area was $37.6\ m^2$ with a design membrane flux of $25\ L/\ m^2.h$ and a maximum membrane flux of $45\ L/\ m^2.h$. It was operated on the outside – In mode with a pore size of 0.04 µm nominal. Surface water contained turbidity of approximately 100NTU. Ferric chloride was used as the primary coagulant. The system performance was evaluated by measuring dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm (UV_{254}) and membrane permeate flux. Also residual concentration of metal ion (Fe) in permeate was determined.

The results showed that regardless of the raw water turbidity, the membrane permeate water turbidity was always below 0.1 NTU. The hybrid system removed DOC more efficiently than the conventional water treatment process, and the removal percentage by the hybrid system was in the range of 34–54%. The membrane permeability improved greatly with the inclusion of citric acid as part treatment chemical for chemical cleaning in place (CIP). Pre-treatment with coagulation not only improved the treated water quality, but also enhanced membrane performance, that is, the permeate flux increased and flux decline was reduced.

Ultrafiltration of surface water with PVDF membranes was proven very useful for drinking water production. The results of this study have shown that ultrafiltration membrane can be applied to impounded water treatment for public supply from the viewpoint of treatment efficiency and effectiveness of contaminant rejection.

89 Role of Permeate Flux and Specific Membrane-Foulant-Solute Affinity Interactions (°¼ΔG°½_slm) in Transport of Trace Organic Solutes through Fouled Nanofiltration (NF) Membranes.

Oranso T. Mahlangu[1]*, Klaas V. K. M. Schoutteten*[2]*, Arnout D'Haese*[2]*, Bhekie B. Mamba*[3]*, and Arne R. Verliefde*[4]
(1)Nanoscience and Water Sustainability (NanoWS), University of South Africa, Johannesburg, South Africa, (2)Ghent University, Ghent, Belgium, (3)School of Science, Engineering and Technology, University of South Africa, Johannesburg, South Africa, (4)Applied Analytical and Physical Chemistry, University of Ghent, Ghent, Belgium

90 Behavior of Oil Droplets at the Membrane Surface during Crossflow Microfiltration of Oil-Water Emulsions.

Emily Tummons[1], *Volodymyr Tarabara*[1], *Anthony G. Fane*[2], *and Jia Wei Chew*[3]
(1)Civil and Environmental Engineering, Michigan State University, East Lansing, MI, (2)Singapore Membrane Technology Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, Singapore, Singapore, (3)School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore, Singapore

Mixed Matrix Membrane for Protein Separation (oral).

Junfen Sun
Donghua University, Shanghai, China

In this study, strontium-substituted nano hydroxyapatite (Sr-HAP) was synthesized by ultrasonic method. The surfaces of Sr-HAP particles were grafted with acrylic acid (AAc) by low temperature plasma technology and Sr-HAP grafted with AAc (Sr-HAP-AAc) was obtained. The dual layer polyether sulfone (PES)/HAP mixed matrix membranes (MMMs) were prepared by an immersion phase separation process. A particle free PES membrane layer was co-cast with the active support layer, which led to formation of dual layer MMMs. The active support layer consisted of Sr-HAP-AAc particles embedded in macroporous PES. The dual layer MMMs showed separation of protein via diffusion as well as adsorption. The bovine serum albumin (BSA) was used as a model protein. The BSA adsorption capacity of MMMs increased with extending equilibrium time and almost reached stable at 20 h. The BSA adsorption capacity of dual layer MMMs was 48.6 mg/(g MMMs). The dual layer MMMs with top PES layer kept good filtration and adsorption properties.

MOLECULAR SEPARATION AND PERVAPORATION

92 Organic Solvent Reverse Osmosis: Formation of Solvent-Resistant Asymmetric Carbon Molecular Sieve Hollow Fiber Membranes.

Dong-Yeun Koh[1], *Melinda L. Jue*[1], *Benjamin A. McCool*[2], *Harry W. Deckman*[2], *and Ryan P. Lively*[1]
(1)School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA, (2)ExxonMobil Research and Engineering, Annandale, NJ

PEEK Hollow Fiber Composite Gas Separation Membranes Applied in Minimal Pretreatment and Condensing Environments.

***Yong Ding**, Benjamin Bikson, James Macheras, and Joyce Nelson*
Air Liquide Advanced Separations, Woburn, MA

Poly(ether ether ketone), PEEK, is a semi-crystalline, high performance engineering polymer, well known for its solvent/chemical resistance and a high temperature operating capability. The excellent chemical and physical characteristics of PEEK make it an ideal candidate for the preparation of the next generation of polymeric membranes that combine inorganic membrane robustness with polymeric membrane performance and price.

PEEK hollow fiber membranes were successfully developed and commercialized by melt extrusion of compatible PEEK/polyimide blend, . The polyimide in the blend serves as a pore former and is quantitatively removed to produce the target porous PEEK membrane. Membrane morphology and pore size is controlled by the blend composition and processing conditions. The methodology is highly flexible and provides for preparation of both flat sheet and hollow fiber membranes. PEEK exhibits thermo-mechanical properties superior to almost all engineering polymers currently in use in membrane preparation.

A family of composite hollow fiber membranes based on PEEK have been developed and commercialized for variety of natural gas purification applications, such as BTU reduction, H2S and CO2 removal. PEEK based hollow fiber membranes are extremely robust. The membrane separation performance is not affected by the presence of organic liquids, such as NGLs. Only coalescing filter pretreatment is required for all commercial PEEK membrane systems. The elimination of the extensive pretreatment significantly reduces the capital cost and maintenance cost. One example of the use of the PEEK hollow fiber membrane is for H2S reduction. Application of the PoroGen™ membrane portfolio to multiple industrial application will be presented.

94 Spent IPA Dehydration for in-House Reclamation.

***Yu (Ivy) Huang**[1], Richard Baker[2], Yan Gao[3], Ramin Daniels[4], and Xuezhen Wang[2]*
(1)Membrane Technology & Research, Inc., Menlo Park, CA, (2)MTR, Newark, CA, (3)Membrane Technology & Research, Newark, CA, (4)Membrane Technology and Research, Inc., Newark, CA

95 Aromatic Polyimide and Crosslinked Thermally Rearranged Poly(benzoxazole-co-imide) Membranes for Isopropanol Dehydration Via Pervaporation.

Yi Ming Xu[1], *Ngoc Lieu Le*[2], *Jian Zuo*[1], *and Tai-Shung Chung*[1]
(1)Chemical and Biomolecular Engineering, National University of Singapore, Singapore, Singapore, (2)Biological and Environmental Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia

97 A New Molecular Approach to Tuning Separation Properties of Carbon Molecular Sieves.

Graham Wenz[1] *and William J. Koros*[2]
(1)School of Chemical and Biolmolecular Engineering, Georgia Institute of Technology, Atlanta, GA, (2)School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA

98 Electric Field-Assisted Membranes for Molecular Separation.

Oleg Polyakov
Thermosolv LLC, Laramie, WY

Highly-Efficient Immersion Engineering of PEO Membranes Toward Superior CO2 Separation Performance.

Lu Shao *and Shuai Quan*
Harbin Inst Technol, Harbin, China

Herein, we designed an extremely versatile strategy to significantly improve gas transport properties of PEO-containing cross-linked membranes based on their specific swelling properties. Low-molecular-weight poly (ethylene glycol) (PEG) was deliberately incorporated into synthesized swellable pure PEO cross-linked membrane via immersing PEO membrane into PEG-water solution and membranes with various PEG loadings are obtained. The imbedded PEG molecules can be located between polymer chains to improve chain mobility and increase chain distance, resulting in the increase of fractional free volume (FFV), which is in favor of gas diffusion. For example, the flexible incorporation of low-molecular-weight poly(ethylene glycol) dimethyl ether (PEGDME) into the swollen network membrane greatly improved the gas transport performance and

the CO_2 permeability was increased by **550%**. The separation performance was correlated nicely with the microstructure of the membranes. This study may provide useful insights about the formation and mass transport behaviour of highly-efficient polymeric membrane applicable to clean energy purification and CO_2 capture, and possibly bridge the material-induced technology gap between academia and industry. Most importantly, our discovered strategy has great potential for treating composite membranes and regenerating "aged" membranes to realize clean energy purification and CO_2 capture by membrane technology.

NAMS AWARD SESSION

99 Optimizing Hollow Fiber Membranes and Modules for Osmotic Processes: From Models to Membranes to Modules.

Jian Ren *and Jeffrey McCutcheon*
Department of Chemical and Biomolecular Engineering, University of Connecticut, Storrs, CT

101 Fundamental Studies of Ion Sorption and Transport in Ion-Exchange Membranes.

Jovan Kamcev*, Benny D. Freeman, and Donald R. Paul*
McKetta Department of Chemical Engineering, The University of Texas at Austin, Austin, TX

102 Antibody Purification from Cell Culture Supernatant Using New Multimodal Membranes.

Juan Wang[1] *and Scott M. Husson*[2]
(1)Chemical and Biomolecular Engineering Department, Clemson University, Clemson, SC, (2)Chemical and Biomolecular Engineering, Clemson University, Clemson, SC

103 Poly(ionic liquid)/Ionic Liquid Ion-Gel Membranes for CO_2/Light-Gas Separations.

Matthew G. Cowan[1]*, William M. McDanel*[2]*, Trevor K. Carlisle*[3]*, Zoban V. Singh*[4]*, Douglas L. Gin*[4,5]*, and Richard D. Noble*[2]

(1)Department of Chemistry & Biochemistry, University of Colorado, Boulder, CO, (2)Dept. of Chemical and Biological Engineering, University of Colorado at Boulder, Boulder, CO, (3)Dept. Chemical and Biological Engineering, University of Colorado at Boulder, Boulder, CO, (4)Department of Chemical and Biological Engineering, University of Colorado, Boulder, CO, (5)Dept. of Chemistry & Biochemistry, University of Colorado at Boulder, Boulder, CO

Engineering Nanostructured Ion-Containing Block Polymers for Membrane Separation Applications.

Matthew D. Green
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Membrane-mediated transport has industrial and commercial applications in food packaging, water and gas separation, energy storage and harvesting, performance clothing, sensors, and many others. However, decoupling conflicting constraints is commonly necessary; for example, water purification and gas separation membranes frequently suffer from the permeability-selectivity trade off. Ion-containing block polymers offer a design strategy to decouple transport from thermomechanical performance: membranes that form transmembrane or bicontinuous microphase separated morphologies enable transport through the ionomer phase while the surrounding microphase(s) provide robust mechanical properties. This presentation will focus on strategies for preparing and the performance of ion-containing block polymer membranes with bicontinuous morphologies and percolated transport pathways.

104 Membrane Performance Characterization and Process Prediction in Osn: Challenges, Achievements and Perspective.

Patrizia Marchetti[1], *Binchu Shi*[2], *Dimitar Peshev*[3], *and Andrew Livingston*[1]
(1)Chemical Engineering, Imperial College London, London, United Kingdom, (2)Evonik MET Ltd., London, United Kingdom, (3)University of Chemical Technology and Metallurgy, Sofia, Bulgaria

NOVEL MEMBRANE MATERIALS I

106 Polymer Nanofilms with Enhanced Microporosity By Interfacial Polymerisation for Molecular Separations.

Maria F. Jimenez Solomon[1]*, Qilei Song*[1]*, Kim E. Jelfs*[2]*, Marta Munoz-Ibanez*[1]*, and* ***Andrew G. Livingston***[3]
(1)Department of Chemical Engineering, Imperial College London, London, United Kingdom, (2)Department of Chemistry, Imperial College London, London, United Kingdom, (3)Chemical Engineering, Imperial College London, London, United Kingdom

Novel Polynorbornenes for Gas Separation Membranes.

Benjamin J. Sundell*, John A. Lawrence III, Daniel J. Harrigan, Justin T. Vaughn, and Tatiana Pilyugina*
Boston Downstream Research Center, Aramco, Cambridge, MA

Saudi Arabia produces approximately half of its domestic electricity from natural gas. With nearly 300 trillion standard cubic feet in proven natural gas reserves, a small fraction of those reserves has low BTU content. Gas separation membranes have the potential to help monetize these low BTU content reserves, but there are still challenges with membrane technologies for these applications. To address these challenges, a systematic series of novel polynorbornenes with varying substituents were synthesized. Structural evidence via NMR and FTIR demonstrate the role that substituent *endo-exo* isomerism has on resulting polymeric microstructure, yield, and permeation properties. Substitution also enables covalent crosslinking via tunable sol-gel routes that helps to stabilize the membranes. This talk will describe how X-ray diffraction has been used to provide a unique perspective into the porosity and crosslinking of these materials and to demonstrate that pendant substitution can be a successful technique to increase intermolecular spacing, a paradigm for further improving selectivities. Finally, both pure and mixed gas permeation studies have revealed that substitution can double gas separation selectivities compared to unmodified polynorbornene while retaining high gas permeabilities, further demonstrating the promise of these novel membranes for gas separation applications.

107 Highly Permeable Peptide-Appended Pillar[5]Arene Artificial Water Channel in Block Copolymer Membranes.

Yuexiao Shen[1]*, Tingwei Ren*[2]*, Daniel Tsai*[2]*, Ian Sines*[2]*, and Manish Kumar*[3]
(1)Department of Chemical Engineering, The Pennsylvania State University, University Park, PA, (2)Pennsylvania State University, (3)Department of Chemical Engineering, Pennsylvania State University, University Park, PA

Zwitterion-Containing Polymer Additives for Fouling Resistant Ultrafiltration Membranes: Choosing the Right Chemistry and Architecture.

Ayse Asatekin
Department of Chemical Engineering, Massachusetts Institute of Technology,
Cambridge, MA

Fouling is likely the most significant obstacle to the wider use of membranes in many processes, especially when the feed contains large quantities of organic contaminants such as proteins, natural organic matter, and oil. Zwitterions, which have equal numbers of positively and negatively charged groups, are very hydrophilic and strongly resist fouling. Blending a zwitterion-containing polymer with a commodity polymer such as polyvinylidene fluoride (PVDF) during membrane manufacture by non-solvent induced phase inversion (NIPS) is a promising approach to making fouling resistant ultrafiltration (UF) membranes. It does not require any post-processing steps and can be plugged directly into existing membrane manufacturing facilities. A handful of studies demonstrate varying degrees of fouling resistance when zwitterion-containing amphiphilic copolymers are blended with PVDF to prepare membranes. However, we do not know how copolymer chemistry, architecture, and blending ratio with the base polymer affect final membrane properties. There are no guidelines on how to design and select a zwitterion-containing copolymer for optimal performance. In this study, we seek to identify the effect of several copolymer features on the performance of membranes prepared from its blends with PVDF: Zwitterion chemistry, hydrophobic monomer chemistry, copolymer composition (i.e. zwitterionic/hydrophobic monomer ratio), copolymer architecture, and blend composition. We synthesized several copolymers varying these parameters, and evaluated the morphology, permeance, selectivity and fouling resistance of resultant membranes. We have found design rules to direct the selection of best polymer structures and architectures for this use. First, we found that unlike past reports, a higher hydrophilic/zwitterionic monomer content in the copolymer does not necessarily lead to better performance. Copolymers with high zwitterion contents macrophase separate from PVDF during the NIPS process. The resultant membrane has poor performance. Second, we can identify the copolymer compositions where this problem will be avoided using thermal analysis of copolymer/PVDF blends. If the copolymer leads to a shift in the glass transition temperature of PVDF, this predicts good anchoring of the copolymer and improved fouling resistance. Third, even very small quantities of zwitterion-containing copolymers can lead to significant increases in permeance and exceptional fouling resistance. As little as 5 wt% zwitterionic copolymer can lead to 6x higher flux with little change in rejection, and show essentially complete resistance to irreversible fouling. Finally, this effect is more prominent with comb-shaped copolymers with the zwitterions are arranged as short side-chains attached to the hydrophobic backbone, in comparison with random copolymers of the same repeat units. This information is crucial for membrane companies considering such copolymer additives to improve the performance of PVDF membranes, enabling rational design of zwitterion-containing polymers for membrane applications. We are currently further exploring the responsive and self-cleaning properties of these membranes, and their performance in realistic applications such as wastewater treatment.

Crosslinked Polytriazole Membranes for Organophilic Filtration.

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(1)Biological and Environmental Sciences & Engineering Division (BESE), King Abdullah University of Science & Technology (KAUST), Thuwal, Saudi Arabia, (2)University of Bologna, Bologna, Italy

Pharmaceutical and chemical industries generate a large amount of organic solvents which need to be recovered for further use, otherwise will become waste solvent. Membrane technology can be used as an alternative process to more conventional separation methods with advantage of low energy consumption.

In this study we report the facile synthesis of new crosslinked polytriazole membranes for organophilic filtration by using poly(ethylene glycol) diglycidyl ether (PEGDE), which is not toxic and cheap crosslinker. The polytriazole is highly soluble in common organic solvents due to the presence of 98% of free OH groups, which can be easily processed by a phase inversion method. The resulting membranes are stable in wide range of organic solvents and in all range of pH. The THF flux is 49 L m^{-2} h^{-1} bar^{-1} for the membrane with MWCO of 6.9 kDa and 17.5 L m^{-2} h^{-1} bar^{-1} for the membrane with a MWCO of 2.8 kDa. By using different casting solution and different crosslinking time it is possible to tailor the MWCO of crosslinked polytriazole membranes to cover the range from the lower end of ultrafiltration to upper end of nanofiltration, indicating that these membranes can be used in wide range of applications.

Acknowledgement

This research was supported by King Abdullah University of Science and Technology (KAUST)

Adsorption of Polyelectrolyte Multilayers Imparts High Monovalent/Divalent Cation Selectivity to Nafion and Fujifilm Cation-Exchange Membranes.

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Although commercial ion-exchange membranes show high selectivities between cations and anions, they have modest selectivities among monovalent and divalent cations or monovalent and divalent anions. Such selectivities among cations or among anions are important, however, in applications such as purifying salts. This presentation will describe layer-by-layer adsorption of polyelectrolytes on cation-exchange membranes to impart extreme selectivities among monovalent and divalent cations. Deposition of protonated poly(allylamine) (PAH)/poly(4-styrenesulfonate)(PSS) films on Nafion membranes leads to K^+/Mg^{2+} electrodialysis selectivities >1000. Unfortunately, the current efficiency is only 0.5, so unwanted ions (such as protons) carry 50% of the current. Moreover, the high price of Nafion membranes (\$800 for 0.5 m^2) limits their practical application. We recently found that $(PAH/PSS)_5PAH$-modified Fujifilm cation-exchange membranes show a K^+/Mg^{2+} electrodialysis selectivity of ~800 with a current efficiency of 0.5. The corresponding unmodified membranes show selectivities <2. The Fujifilm substrates do not contain expensive fluorinated polymers and are thus much less expensive than Nafion. To increase current efficiency, we coated Nafion membranes with polydiallyldimethylammonium (PDADMAC)/PSS films. $(PDADMAC/PSS)_5PDADMAC$-modified Nafion membranes exhibit K^+/Mg^{2+} and Li^+/Co^{2+} selectivities > 1000, but in Li^+/Co^{2+} separations, the current efficiency is 0.6 for $(PDADMAC/PSS)_5PDADMAC$-modified Nafion and only 0.45 for $(PAH/PSS)_5PAH$-modified Nafion. The higher current efficiency may stem from swelling of PDADMAC/PSS films. However, the PDADMAC/PSS films likely delaminate at high ionic strength, so we are working on cross-linking chemistries to stabilize these membranes.

NOVEL MEMBRANE MATERIALS II

109 Sorption Enhanced Mixed Matrix Membranes for High Temperature H2/CO2 Separation.

Lingxiang Zhu*, Deqiang Yin, Shailesh Konda, Mark Swihart, and Haiqing Lin*
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Abstracts:

- Abstract for NAMS 2016.docx (20.8KB) - Abstract Text

110 Fabricating Nanoporous Metallic Films As Components of Composite Membranes.

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Abstracts:

- Abstract Mike np_PdFe_NAMS 2016.docx (14.0KB) - Abstract Text

111 Tuning PIM-PI-OH/Z-MOF-Based Mixed-Matrix Membranes for Highly Efficient C3H6/C3H8 Separation.

Ramy Swaidan[1]*, Xiaohua Ma*[2]*, and Ingo Pinnau*[1]
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Exploring the Potential of Nanoporous Single-Layer Graphene As a Next-Generation Membrane Material.

Rohit Karnik
Massachusetts Institute of Technology, Cambridge, MA

Nanoporous graphene has potential as an ideal ultrathin membrane for high-flux, high-selectivity, chemically-resistant membrane separations. I will discuss our work on understanding mass transport and developing membranes that employ nanoporous single-layer graphene as the selective layer. Through controlled nucleation of defects *via* ion bombardment and oxidative etching, sub-nanometer pores are created in the otherwise impermeable graphene placed on a porous support. The resulting membranes exhibit selectivity between ions and between salt and small molecules. We also present strategies for the design of defect-tolerant membranes using centimeter-scale areas of single-layer graphene, which allows for measurement of water flux and solute rejection during filtration by forward osmosis. The membrane can reject multivalent ions and small molecules, and exhibits a permeance that is consistent with theoretical predictions. We also demonstrate that these membranes exhibit high mechanical strength and are able to withstand applied pressures up to 100 bar. These studies illustrate the feasibility and potential of single-layer nanoporous graphene membranes for nanofiltration, water purification, and other applications.

Separation of Chiral Molecules Using Mixed Matrix Membranes Incorporating Chiral Metal Organic Frameworks.

Bradley P. Ladewig*, Benjamin Slater, and Marine Michel*
Department of Chemical Engineering, Imperial College London, London, United Kingdom

Exciting new porous coordinated materials have recently been synthesised that incorporate chiral pore structures, which opens up the opportunity to use these materials as sorbents for the selective adsorption of enatiomerically distinct molecules from racemic mixtures. The significance of this development to the pharmaceutical and fine chemical industries is enormous, since a significant proportion of their products are chiral molecules which are usually separated using low-throughput, highly expensive elution columns (or must be synthesised using challenging chemistry which is directed towards producing enantiomerically pure products).

In this presentation, we will outline our recent results synthesising chiral metal organic framework materials using two distinct approaches; the use of chiral ligands to impart chirality to the resulting metal organic framework, and an emerging and lower-cost approach with is to post-synthetically modify non-chiral (but usually easily synthesised) subtrate materials, to impart a degree of chirality to them. These materials are tested as batch liquid-phase sorbents to screen their potential for selective sorption of a library of low molecular weight chiral molecules (primarily sugars, alcohols and amino acids). The most promising candidates, are incorporated into mixed matrix membranes and tested as membranes, with a specially- configured gas chomatograph with chiral columns used to resolve the components in the feed and permeate, to quantify the selectivity.

CNT Membranes with Sub-Nm Pores Showing Salt Rejection and Sharp Size Selectivity at High Ionic Strenghts.

Rob McGinnis[1]*, Kevin Reimund*[2]*, Kevin A. Stevens*[3]*, Joshua Moon*[4]*, Benny D. Freeman*[3]*, Jian Ren*[5]*, Lingling Xia*[5]*, and Jeffrey McCutcheon*[5]
(1)Nagare Membranes, New York, NY, (2)Nagare, New York, NY, (3)McKetta Department of Chemical Engineering, The University of Texas at Austin, Austin, TX, (4)Univ of Texas, Austin, TX, (5)Department of Chemical and Biomolecular Engineering, University of Connecticut, Storrs, CT

Abstract: We report water and gas separation performance for novel carbon nanotube (CNT) membranes consisting of the smallest (0.67 - 1.27 nm inner diameter) single wall nanotubes yet reported for CNT membranes. The CNTs traverse a non-porous, non-water-permeable, flexible polymer film, and show rejection of small salts at high ionic strength, and highly specific size selectivity for sub-1.5 nm solutes. Water flow through the membranes showed significant enhancement over that predicted by Hagen-Poiseuille flow, in agreement with previous CNT membrane studies. Gas selectivity was found to be similar to that predicted by Knudsen flow for non-condensable gases, but the permeabilities were found to be significantly higher than those predicted by Knudsen, also in agreement with previous studies of CNT membranes. CO2 permeation was found to be substantially higher than predicted. The membranes used in this study were fabricated using non-aligned bulk CNTs, orientated during membrane formation to give a membrane with tubes traversing a non-porous polymer film. Membranes of this type will allow for the use of very small diameter nanotubes previously not suitable for use in CNT membranes, offering the potential to perform separations of sub-nm solutes with angstrom-scale selectivities.

112 Carbon Molecular Sieve Membranes for Mixed Olefins/Paraffins Separations.

Yu-Han Chu *and William J. Koros*
School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA

PLENARY LECTURE: DR. MICHAEL YANDRASITS

N/A Fuel Cell Membranes based on Perfluorsulfonic Acids and.

Michael Yandrasits
AL

PLENARY LECTURE: DR. WINSTON HO

Recent Developments on Membranes for CO2 Separation and Water Purification.

Winston Ho
Chemical and Biomolecular Engineering, The Ohio State University, Columbus, OH

POSTER PRESENTATION I - ENERGY AND ENVIRONMENT

113 High-Throughput Hollow-Fiber (HT-HF) Membrane Module – a Miniaturized, Parallel Format Approach Ideal for the Accelerated Design of Environmental Separation Processes.

Amir S. Kazemi, Seung Mi Yoo, Raja Ghosh, and ***David R. Latulippe***
Chemical Engineering, McMaster University, Hamilton, ON, Canada

Iron Nanoparticle Functionalized Membrane for PCB Degradation from Water - Poster.

Hongyi Wan[1]*, Minghui Gui*[2]*, Lindell Ormsbee*[3]*, and D.B. Bhattacharyya*[2]
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The development of functionalized membranes with catalytic metal nanoparticles provides an effective method of environmental remediation and wastewater treatment. Polyvinylidene fluoride (PVDF) is an excellent polymer for both chemical and mechanic resistance as well as thermal stability. By immobilizing zero-valent iron (ZVI) or bimetallic nanoparticles (NPs), functionalized PVDF membranes can be used in chlorinated organic treatment. Polyacrylic acid (PAA) was polymerized inside PVDF membrane pores to maximize iron adsorption. Adsorbed iron was reduced to form NPs in-situ in order to prevent metal ion loss, NPs aggregation and iron precipitation. Furthermore, tunable membrane pore size could be achieved by changing the environmental pH because of ionization of PAA.

This study includes three major aspects: 1. Reactivity toward model toxic chlorinated organic compounds--polychlorinated biphenyl (PCBs) in both batch and convective flow study; 2. NPs characterization of its average sizes, composition, extent of oxidation and distribution inside membrane pores; 3. Simulating pH responsive behavior and PCB reaction within the membrane.

PCBs are not biodegradable and tend to cycle between air, water and soil, which might accumulation in living organisms. PCBs dechlorination can be achieved by Fe/Pd reductive pathway. The hydrogen, generated from reaction between ZVI and water, gets activated by Pd for hydrodechlorination. In batch study, 95% of PCB 126 ([Co]=15 μM) was consumed and 67% was converted to biphenyl in 5 hours. In convective flow study, 96% of PCB 126 was consumed at 26s residence time. However, the final product biphenyl still showed toxicity. In order to degrade biphenyl, the further oxidative pathway was combined to break down the aromatic ring and eventually form organic acid. Both iron oxide with H_2O_2 method (Fenton Reaction) and persulfate method significantly reduced toxicity of the products of PCB degradation.

Fe/Pd NPs size distribution was analyzed by SEM and TEM (TEM samples were prepared by Focus Ion Beam) and the average size of NPs was 19.4±3.2nm. Iron core and discontinuous palladium shell was tested by STEM-EELS line scan and elemental mapping and extent of oxidation was studied by XRD. Furthermore, membrane permeability change from 32.2LMH/bar to 1.1LMH/bar when environmental pH change from 2 to 6.5. The pH-responsive behavior was simulated and fitted with experimental data, which is a part of PCBs reactivity model.

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114 Physicochemical and Photocatalytic Properties of Carbonaceous Char and Titania Composite Hollow Fibers for Wastewater Treatment.

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115 Evaluation of Different Membrane Separation Processes for Treatment of Acid Mine Drainage and Mine Effluents.

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Organic Acids and Water Membrane Separations from Bio-Oil.

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Over 70% of the world's energy consumption is provided from fossil fuels and with their reserves depleting at a fast rate, alternative energy sources or methods are needed to provide the world's energy needs. This research hopes to aid with the alternative energy needs by making it economically feasible to produce fuel products, such as bio-diesel, from the upgrading of bio-oil obtained from the pyrolysis of biomass waste material such as sawdust. The high water and oxygenated compound content of the bio-oil make it undesirable for fuel use, but by means of a surface modified commercial membrane we hope to facilitate the separation of desired compounds from others which may be used synthesize other commercially useful products. In this research two methods were used for this separation: electrodialysis and a pressure driven system. Physically modified Nafion 117 nanofiltration pore size membranes were used for the pressure driven system in hopes of separating water and low molecular weight compounds from the bio-oil. And anion exchange membranes with added polyethylenimine groups to the membrane surface were used to remove organic acids from the bio-oil. The electrodialysis experiments results showed a decrease in conductivity giving supporting belief that some if not all of the organic acids are were removed. And the procedure to widen the Nafion 117 membrane pores also proved to be successful. With Nafion's proven chemical resistance to the bio-oil, it is expected to achieve the desired separation upon obtaining the appropriate pore diameter of the membrane.

Design Supported Ruthenium Catalysts for the Catalytic Oxidation of (chloro)-Benzene.

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Ruthenium-based catalysts are commonly known for their roles in the Fischer-Tropsch synthesis as well as the synthesis of ammonia, and these catalysts have also been applied industrially for chlorine gas production via the Deacon Process. Recently, the catalytic properties of ruthenium-based catalysts in the catalytic oxidation of light alkanes and (chloro)-aromatics have attracted significant interest due to their good activities. In this article, we present our work related to design supported ruthenium catalysts for the catalytic oxidation of (chloro)-benzene. In particular, P25-TiO_2, ZrO_2, γ-Al_2O_3 and SiO_2

supported ruthenium catalysts were synthesized and well characterized by XRD, BET, ICP, XPS and TEM. These catalysts were used for benzene oxidation at first. It was found that the Ru/P25-TiO_2 catalyst with inhomogeneous distributed RuO_2 (mainly distributed in the rutile phase of P25-TiO_2) had the best activity among these catalysts. And the total conversion temperature (T_{100}) of benzene over the Ru/P25-TiO_2 catalyst was approximately at 230 °C. Accordingly, the Ru/P25-TiO_2 catalyst was tested for chlorobenzene oxidation. Noteworthy, T_{100} of chlorobenzene over the Ru/P25-TiO_2 catalyst was below 280 °C, and the organic by-products formed during the catalytic reaction completely disappeared when T_{100} of the reactant was achieved. Hence, the Ru/P25-TiO_2 catalyst showed substantial advantages than the other reported catalysts in the catalytic oxidation of chlorobenzene. Based on the results of XPS, the active species of Ru/P25-TiO_2 was described as chlorinated RuO_2. The excellent performance of the Ru/P25-TiO_2 catalyst for chlorobenzene oxidation could be attributed to the good thermal stability of RuO_2 in the rutile phase of P25-TiO_2 and chlorine removal capacity of the active species.

116 Non-Carbon Adsorbent and Oxidation Catalyst for Mercury Removal from Coal-Fired Flue Gas.

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118 Towards Conductive Chemically-Active Membranes: Flavin-Functionalized Fibers and Electrodes Active in Photo-Enhanced Oxygen Evolution.

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Synthesis of Ru-Based Catalysts for Complete Oxidation of Volatile Organic Compounds.

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In this work, low-temperature catalytic oxidation of volatile organic compounds (VOCs) over Ru-based catalysts was presented. The catalysts were prepared using the wet impregnation method, and characterized by ICP, BET, XRD, TEM, and XPS. The catalytic studies demonstrated that P25 supported catalyst contributed the highest activity. Accordingly, Ru/TiO_2(P25) was particularly studied.

Based on the characterizations, we found that ruthenium species exists as ruthenium oxides, which are often hard to observe in TEM micrographs due to their low contrast. Hence, TEM, HR-TEM, and HAADF-STEM charcterizations were conducted. It can be concluded that ruthenium species tend to be distributed on the rutile-TiO2 of P25 due to their similar crystal lattice properties, leading to an inhomogeneous distribution. The catalyst was employed in complete oxidation of different VOCs, including benzene, chlorobenzene, trichloroethene, and methyl bromide. Noteworthy, for chlorinated VOCs, Ru-based catalyst showed apparently better catalytic performance than catalysts, such as Pd or Pt. Additionally, the thermal stability test, anti-moisture test, and byproducts analysis were also conducted, revealing that Ru/TiO_2 is promising for VOCs purifications in industrial plants.

119 Characterization of Biofouling on Forward Osmosis Membranes Used for Long-Term Produced Water Treatment.

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120 Green Modification of Outer Selective P84 Nanofiltration (NF) Hollow Fiber Membranes for Cadmium Removal.

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123 High Performances of Poly(arylene ether sulfone) with Tetra(quaternary ammonium) Group for Solid Alkaline Exchange Membrane Fuel Cell Applications.

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Metal Oxides Film Catalyst for VOCs Degradation Derived from Hydrotalcite.

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Emission of volatile organic compounds (VOCs) from industrial gases is major contributors to air pollution which may pollute the atmosphere directly or indirectly as secondary pollutants, such asozone generation and photochemical smog. VOCs may be also found in non-industrial indoor air environments, which can act as irritants to the human organism and have negative health effects, and cause bad indoor air quality. Catalytic oxidation with high efficiency and less or no byproducts is recognized as an effective method for VOCs degradation. The monolithic film catalyst recently attracted much attention for their advantages of sufficient exposure of active sites with superb heat conduction and recycling. Transition metal oxides (Fe_2O_3, Cr_2O_3,CuO, Co_3O_4, NiO and MnO_2) as a potential alternative of precious metals, have received much attention for their superior properties such as low cost, high resistance to poisoning, good reducibility. Studies reveal that mixed metal oxides (MMO) own higher catalytic activities than single metal oxide, even equivalent or better than precious metal because of the synergistic effect. To design smartly catalysts with large surface area ratio, rich oxygen species and low temperature reducibility will lead outstanding catalytic activity.

Layered double hydroxides (LDH) are a class of naturally occur-ring and synthetic materials generally expressed by the formula$[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2](A^{-})_{x/n}\cdot$ mH2O, in which M^{II} and M^{III} cations disperse in an ordered and uniform manner in brucite-like layers, and A^{n-} is a charge compensating anion such as NO_3^{-},$\cdot CO_3^{2-}$. The cation composition of LDH-related mixed oxide catalysts can be simply adjusted during precursor synthesis. After heating at moderate temperatures, the resulting mixed oxides catalysts from a topotactic transformation of LDH give finely dispersed mixed oxides of M^{II} and M^{III}metals with a sufficiently large surface area and good thermal stability. LDHs can in situ grow into thin film over varied substrate with hexagonal laminar structure stick to the substrate under proper synthetic condition. Furthermore, the synergistic effect due to the good interspersion of the oxide phases would possess some desirable features, like low temperature reducibility and more lattice oxygen for the improvement of catalytic activity. Besides, the presence of LDH matrix inhibits the agglomeration of active components and thus enhances the long-term stability.

The monolithic transitional metal oxides film catalysts were obtained from the calcination of the in situ growth of the corresponding LDHs precursor on aluminum substrates with nearly 1.32 mg/cm^2 by weight. CoMnAl-MMO sample displays the temperature of 90% benzene conversion (T_{90}) 240 ºC with reaction rate 1.19 mmol g_{cat}^{-1} h^{-1} and space velocity 300,000 mL g_{cat}^{-1} h^{-1}, which is higher than CoNiAl-MMO at 275 ºC and CoCuAl-MMO at 315 ºC.

124 **Investigation of Ultrafiltration,Nanofiltration,Biofiltration and Ozonation for the Removal of Microcystin from Water.**

Joyner Eke, *Priyesh Wagh, and Isabel Escobar*
University of Kentucky, Lexington, KY

125 **Fundamental Studies of Ion Transport in Ion-Exchange Membranes.**

Jovan Kamcev, *Donald R. Paul, and Benny D. Freeman*
McKetta Department of Chemical Engineering, The University of Texas at Austin, Austin, TX

Characterization of Poly(ether ether ketone) Anion Exchange Membrane for Fuel Cell Application.

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In this study, we synthesized a novel poly(ether-ether-ketone), containing di(quaternary ammonium) hydroxide groups in the polymer chain. Then we tested the alkaline-exchange properties of a membrane made from the novel polymer, for fuel-cell applications. First, we synthesized a di-hydroxide monomer with amine groups, which were then converted to ammonium functional groups by immersion in hydroxide solution. Then, we synthesized poly(ether-ether-ketone) using a synthesized monomer and bisphenol A. We controlled the mole ratio of the quaternary ammonium hydroxide groups in the polymer structure to evaluate the performance of the membrane. The performances of polymer-electrolyte membranes with differing degrees of amination were compared. The optimum composition of the membrane was determined based on the chemical and thermogravimetric analyses, mechanical properties, the behavior of water in the membrane, and the level of ion conductivity.

Techno-Economic Assessment of the Closed Loop Osmotic Heat Engine Utilized As an Energy Storage System.

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Osmotic power harnesses the energy of mixing between high salinity and low salinity streams to generate useful energy. The closed loop osmotic heat engine (OHE) is a membrane-based energy cycle that couples pressure retarded osmosis (PRO), an osmotically driven membrane process, with membrane distillation (MD), a thermally driven membrane process. The OHE is unique in that it can be designed to store energy that can be released as needed, for example during periods of peak electricity demand.

High power density in PRO is essential to minimize equipment costs and parasitic pumping losses. Likewise, high water flux is needed in MD to efficiently reconcentrate the diluted draw solution from the PRO process and minimize equipment costs. The objective of this study was to assess the technical and economical potential of the OHE as an energy storage system, and to evaluate several ionic organic and inorganic draw solutions as working fluids in the OHE. The performance of select working fluids was assessed in terms of PRO power density and reverse solute diffusion, and MD water flux and thermal efficiency. Potential pore wetting of the MD membrane was also evaluated. The working fluids were also assessed in terms of their potential for equipment corrosion.

Results indicate that sodium formate and calcium chloride draw solutions outperform sodium chloride draw solution (commonly used PRO draw solution) in terms of PRO power density and reverse solute diffusion, and that lithium chloride and calcium chloride outperform sodium chloride in terms of MD water flux. Results were used to perform a techno-economic analysis and make future recommendations on the most suitable working fluid for the OHE as a potential energy storage device. Experimental data and previously established MD and PRO models were used to develop an OHE system model that calculates system efficiency, net power output, and electricity generation costs. Modelling results indicate that with future system improvements, specifically implementation of next generation PRO membranes, the system could be competitive with alternative energy storage technologies.

Nanoporous Silica Membranes for Flow Battery Applications.

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Chemical Engineering, University of Washington, Seattle, WA

Grid-scale power storage remains one of the largest challenges to wide-spread adoption of clean energy technologies with intermittent energy sources (*e.g.,* solar, wind and tidal). Flow batteries are a low cost technology with the potential to meet this need. However, ion exchange membranes that are crucial to battery performance are expensive, lack chemical stability in a strongly oxidizing environment, and have poor ion selectivity which leads to electrolyte diffusion across the membrane and performance instability. In this talk, we discuss the use of a primarily inorganic membrane structure created using liquid glass (*i.e.,* nanoporous silica). Silica is an advantageous material for membranes because of its excellent chemical stability and extremely low cost. Furthermore, the liquid glass curing process produces an average pore radius of ~ 3 nm which allows for effective size exclusion of electrolytes (*i.e.,* low permeability). In this study, small angle neutron scattering (SANS) was utilized to characterize the membrane pore structure. Proton conductivity and vanadium permeability were also determined and compared to Nafion 117. Silica membranes showed similar performance attributes to Nafion, including ion selectivity. These promising results, and routes towards performance enhancements, are discussed.

126 Correlating Nafion Membrane Microstructure with Vanadium Redox Flow Battery Performance.

Wei Wang
Pacific Northwest National Laboratory, Richland, WA

127 Maximizing Yield, Cost Savings and Environmental Benefits Using Osn Membrane Technology for Efficient Purifications.

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Degradation of Chlorinated Organics By Temperature Responsive Pnipam-Co-PAA Functionalized MF Membranes with Reactive Nanoparticles.

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Degradation of Chlorinated Organics by Temperature Responsive PNIPAm-co-PAA Functionalized MF Membranes with Reactive Nanoparticles

Anthony Saad (speaker), Li Xiao, Minghui Gui, Dibakar Bhattacharyya

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Abstract

This study is aimed at evaluating the effect of temperature on the degradation of chlorinated organics, specifically polychlorinated biphenyl. PVDF microfiltration membranes are functionalized with poly-N-isopropylacrylamide (PNIPAm), and its temperature responsive behavior is studied as it relates to water flux and partitioning of toxic pollutants. Effective pore size can be predicted based on the swelling extent of the temperature-responsive PNIPAm polymer around its LCST. PNIPAm is known to show a sharp transition to a hydrophobic state at its lower critical solution temperature (LCST) at around 32^{o}C, making PNIPAM attractive for industrial applications. Swelling ratios of PNIPAm polymeric networks have been reported in water, and are utilized to estimate changes in both flux and pore diameter.

The entrapment of reactive Fe/Pd nanoparticles in a poly-acrylic acid (PAA) polymer domain has been reported. Here, the NPs are entrapped in the temperature responsive PNIPAm-co-PAA polymer network for dechlorination and contaminant degradation of PCBs. This study aims to evaluate PCB degradation by reactive immobilized nanoparticles in a PNIPAm functionalized PVDF MF membrane. A model is formulated to account for diffusion through the membrane, as well as reactivity of the nanoparticles. Solute concentration is predicted as a function of length through the membrane, and also as a function of time. Increasing the surrounding temperature affects inter-particle spacing and solute adsorption because of the changing PNIPAm conformation, as well as the intrinsic rate constant for the reaction. These effects are predicted, and verified by experimental degradation results. This research is supported by the NIEHS-SRP grant P42ES007380, and by the NSF KY EPSCOR program. Full-scale PVDF membranes were developed through collaborative work with Nanostone-Sepro (Oceanside, CA, USA).

Preparation of a Soluble Poly(ether ether ketone) Anion Exchange Membrane for Fuel Cell Application.

***DeukJu Kim*[1]**, *ChiHoon Park[2], and SangYong Nam[1]*
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We synthesized a novel poly(ether-ether-ketone) containing di(quaternary ammonium) hydroxide groups. Then we tested the alkaline-exchange properties of a prepared membrane for fuel-cell applications. In other to synthesis di-hydroxide monomer with amine groups, we used formaldehyde solution and triethylamine sulotion. And then we synthesized poly(ether-ether-ketone) using a synthesized amine monomer, bisphenol A and difluorobenzophenone. We controlled the mole ratio of the quaternary ammonium

hydroxide groups in the polymer. The performances of membrane with different degrees of amination were compared for the application of the anion exchange membrane.

Nanoporous Silica Membranes for Redox Flow Batteries.

Gregory Newbloom *and Lilo Pozzo*
Chemical Engineering, University of Washington, Seattle, WA

Grid-scale power storage remains one of the largest challenges to wide-spread adoption of clean energy technologies with intermittent energy sources (*e.g.,* solar, wind and tidal). Flow batteries are a low cost technology with the potential to meet this need. However, ion exchange membranes that are crucial to battery performance are expensive, lack chemical stability in a strongly oxidizing environment, and have poor ion selectivity which leads to electrolyte diffusion across the membrane and performance instability. In this poster, we discuss the use of a primarily inorganic membrane structure created using liquid glass (*i.e.,* nanoporous silica). Silica is an advantageous material for membranes because of its excellent chemical stability and extremely low cost. Furthermore, the liquid glass curing process produces an average pore radius of ~ 3 nm which allows for effective size exclusion of electrolytes (*i.e.,* low permeability). In this study, small angle neutron scattering (SANS) was utilized to characterize the membrane pore structure. Proton conductivity and vanadium permeability were also determined and compared to Nafion 117. Silica membranes showed similar performance attributes to Nafion, including ion selectivity. These promising results, and routes towards performance enhancements, are presented.

POSTER PRESENTATION II - WATER TREATMENT AND DESALINATION

129 Comparison of Fouling Mechanisms of Four Nanofiltration Membranes: Optimal Membrane Selection for Stephenfield Regional WTP, MB, Canada.

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An Abrasion-Resistivity Evaluation Protocol for MBR Membranes.

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An Abrasion-Resistivity Evaluation Protocol for MBR Membranes

Polymeric membranes used in MBR operations have deferent chemicals, i.e., CPVC, PVDF, PES, PTFE, etc., on backers usually PET or PP. Since the membrane surface during operation is susceptible to the abrasion by the suspended solids, it’s important to know the resistivity to abrasion when we design the polymeric membranes; otherwise we end up in getting the turbid filtrate. In this study we developed a new protocol for evaluating the abrasion resistivity and compared several membranes in commercial use. Since the protocol is of an accelerating nature, we can even predict the lifespan of each membrane.

Development of Reverse Osmosis Mixed Matrix Membrane Using Water Impermeable Matrix.

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Current osmotic processes offer the potential to increase water recovery from wastewater; however there are two problems with currently available reverse osmosis (RO) membranes. First, the polyamide-based RO membranes rapidly degrade when exposed to acid pretreated urine and urine brines. Additionally, present RO membranes have relatively low rejections (60%) of neutral solutes such as urea[1] while they have very high rejections (>99%) of ionic solutes.

Our research focuses on the development of mixed matrix membranes that solve both problems. We developed an innovative mixed matrix membrane design that integrates water-selective zeolite nanoparticles into a liquid-barrier chemically resistant polymer film.[2] The main distinguishing characteristics of our new membrane design compared with current mixed matrix membranes include: (1) the use of an impermeable polymer matrix enabling us to use a broader range of chemical resistant polymers; (2) the use of zeolite particles with specific pore size ensureing us the high rejection of the neutral molecules since water is transported through the zeolite rather than the polymer; (3) the use of latex dispersions as the polymer matrix source. Latexes are environmentally friendly water based-solutions, sharing the qualities of low volatile organic compound (VOC), low cost, and non- toxicity. In our design, the zeolite particles are anchored to a porous substrate. Then, a liquid-barrier chemically resistant polymer matrix fills the space between the zeolite nanoparticles and binds the zeolite into a versatile nanocomposite thin film.

In this talk, we will discuss our progress on development and synthesis of this novel membrane. We have successfully anchored zeolite nanoparticles to porous substrates. We have studied the effect of the polarity of solvents, leaving group of silane agents, the temperature and time of the silanization reaction on anchoring zeolite nanoparticles to porous substrates. Furthermore, we have developed a novel fundamental understanding of the latex film formation on porous substrates. We investigated the effect that the properties of the latex solution and the properties of the porous substrate have on the formation of defect free films of latexes on porous substrates.[3] Additionally, we will report on the flux and sodium chloride rejection of brackish water, as well as the material characterization, of our new mixed matrix membrane.

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149 Facile One-Step Modification of Membrane Surface Using Hydrophilic Polymers for Wastewater Treatment.

Nima Shahkaramipour*, Sankara Narayanan Ramanan, Cheng Kee Lai, Chong Cheng, and Haiqing Lin*
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The Void Structure of Fully-Aromatic Polyamide and Its Influence on the Effective Thickness of the Barrier Layer and Permeability of TFC Membranes.

Yiqun Liu *and Jian Xu*
SINOPEC Beijing Research Institute of Chemical Industry, Beijing, China

The void structure of fully-aromatic polyamide and its influence on the effective thickness of the barrier layer and permeability of TFC membranes

Yiqun Liu*, Jian Xu

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Abstract

The thickness of the fully-aromatic polyamide (PA) barrier layer of the TFC membrane plays an important role in controlling the water permeability of the membrane. Typically this PA layer is not a homogenous dense layer, and thus the thickness of this separation layer measured with TEM or other characterization techniques is actually an

apparent thickness. Our previous research [1] has proved that the PA layer has complex porous structure. Other researchers [2] also confirmed the existence of voids in the PA active layer and measured the volume fraction of these voids recently. Considering the void structure in the PA layer, the effective thickness of the PA layer through which water really penetrates during the filtration process is much thinner than the apparent thickness. In our opinion, the dense layer near the PA top surface with thickness of ca. 20 nm is the key barrier layer for PA layer possessing pores on its backside due to the connection between the voids with the backside of the PA layer.[1] In this case, the effective thickness of the PA layer with apparent thickness of several hundred nm should equal the thickness of the key barrier layer, ie. ca 20 nm.

In this study, a series of TFC membranes with different void structures in the PA layer were synthesized by only changing the concentration of m-phenylene diamine (MPD) and trimesyol chloride (TMC) respectively. The apparent thickness of the PA layer of these TFC membranes was measured by using SEM, TEM and Film Thickness Probe. The void structure of the PA layer was characterized by observing the morphology of the top surface, cross-section and backside of the PA layer. The effective thickness of the PA layer was analyzed by combining the water permeability results and the membrane void structure. Based on the membrane structure characterization and the membrane permeability performance, the mechanism of the formation of PA layer with different void structures was proposed and discussed.

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150 The Relation Between Structure-Performance of Thin Film Composite Membranes and the Tools Used for Their Fabrication Method.

Kelly Briceño[1], *Irakli Javakhishvili*[2], *Haofei Guo*[3], *Knud Villy Christensen*[1], *Birgir Norddahl*[1], *Søren Hvilsed*[4], *and Frank Lipnizki*[3]
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Gypsum Scaling and Membrane Integrity of Osmotically Driven Membranes: The Effect of Membrane Materials and Operating Conditions.

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The emerging thin film composite (TFC) forward osmosis (FO) and pressure retarded osmosis (PRO) membranes generally have better separation properties compared with their cellulose triacetate (CTA) counterparts. Nevertheless, their scaling performance has been rarely reported. In the current study, the phenomenon of membrane integrity loss as a result of scaling is reported for the first time for osmotically driven membrane processes (ODMPs). The results show that the TFC membrane suffered marked flux reduction during the gypsum scaling in the active-layer-facing-feed-solution (AL-FS) orientation, accompanied with the severe damage of the membrane active layer. The membrane integrity loss is attributed to the scale formation and growth in the confined space between the membrane and the feed spacer. Compared with the CTA membrane, the TFC membrane was more prone to scaling and membrane damage due to its unfavorable physiochemical properties (thin active layer with Ca^{2+} binding sites and ridge-and-valley roughness). Although antiscalant addition was shown to be effective for scaling control in AL-FS, it was ineffective in the active-layer-facing-draw-solution orientation. On the other hand, the important role of spacer in scale formation and membrane surface damage was also observed – membrane damage did not occur in the absence of feed spacer. The current study reveals the critical need for scaling control in ODMP processes with respect to the membrane integrity and flux stability. The results also have far-reaching implications for membrane and spacer design and process operation.

Dual-Functional Coating of Forward Osmosis Membranes for Hydrophilization and Anti-Microbial Resistance.

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Microbial fouling and internal concentration polarization (ICP) are factors limiting the performance of forward osmosis (FO) membranes. These limitations in flat sheet thin

film composite (TFC) FO membranes were mitigated by a single Ag/AgCl nanocomposite coating in this study. The coating was prepared by first adsorbing Ag$^+$ on the negatively charged carboxylate groups of polyacrylic acid (PAA)-polyethersulfone (PES) blend membrane substrate (support layer). Cl$^-$ ions were introduced next to form a conformal AgCl coating in-situ. Irradiation of the coating with visible light then converted it into a composite coating with Ag on the membrane substrate exterior and AgCl in the membrane substrate interior. The Ag/AgCl-coated membranes prepared as such delivered good antimicrobial resistance concurrently with a high water flux. The antimicrobial performance could be attributed to a high loading of nano-Ag on the membrane exterior while the high water flux to the AgCl hydrophilization of the membrane interior which reduces the ICP. To the best of our knowledge, this is probably the first demonstration of a dual-functional coating for FO TFC membranes.

Fouling Resistant and Directly Heatable MD Membranes with Hydrophilic and Conductive Surface.

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Membrane distillation (MD) is promising technique for treatment of waters contaminated with high salt concentration, such as ground water, produced water, and brines generated from desalination. Like all membrane processes, MD suffers from fouling that leads to performance degradation. The hydrophobic nature of the MD membrane surface allows for adsorption of NOM and other organic foulants that clog membrane pores, and can lead to membrane wetting, irreversibly degrading their performance. Here, we present a method of synthesizing composite MD membranes with hydrophilic or hydrophobic conductive carbon nanotube thin film surfaces layered on a hydrophobic MD support. We demonstrate that the hydrophilic surface reduces fouling caused by humic acids, while still maintaining the same performance as a bare MD membrane. Finally, we demonstrate a novel method of generating the thermal driving force in the MD process by heating the carbon nanotube thin film surface directly via joule heating. The direct heating of the MD surface eliminates the need to heat the bulk feed solution, allows for high recovery in single pass, and could significantly reduce the complexity and construction cost of MD plants.

An Polymeric Draw Solute for Energy Efficient Forward Osmosis Based Water Purification.

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152 Facile One-Step Modification of Membrane Surface Using Zwitterionic Polymers for Wastewater Treatment.

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153 Vibrational and X-Ray Spectroscopy and Microscopy Reveal Irreversible Fouling Mechanisms of Reverse Osmosis Membranes during Water Reuse: Direct Evidence of Aluminum Coagulant Carryover.

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The AgCl-Based Mineralized Thin-Film Composites (TFC) Membrane for Forward Osmosis.

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The AgCl-based mineralized thin-film composites (TFC) membrane for forward osmosis

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Forward osmosis (FO) membrane processes are emerging technologies that have demonstrated great potential in various water treatment applications. FO has many advantages including lower propensity towards fouling, lower energy, high water flux, high recovery and high quality product. However, FO still faces some critical challenges such as concentration polarization and chemical tolerance requiring further membrane development. Increasing researches have focused on preparing new FO membranes.

We synthesized novel AgCl-based mineralized thin-film composites (TFC) as forward osmosis (FO) membranes. We deposited silver chloride on the surface of the hand-cast polysulfone/polyamide (PSf/PA) membranes through surface mineralization by an alternate soaking process (ASP) in which we repeatedly dipped the membrane into aqueous solutions of silver nitrate ($AgNO_3$) and sodium chloride (NaCl). We synthesized membranes with different mineralization degrees (MD) by changing the number of ASP cycles. We use SEM, EDS, AFM, Contact angle, etc. to characterize the FO membranes. The results of MD, SEM and EDS confirmed the existence of the AgCl coating layer on membrane surface. The results of AFM and contact angle showed the mineralized membrane surfaces were smoother and more hydrophilic. We tested the FO performances of the membranes at 25 □ with pure water as the feed solution and 1 M NaCl solution as the draw solution. We found the mineralized membranes exhibited better water flux and salt rejection than original TFC membranes and the commercial CTA-ES FO membrane. We will choose Bovine Serum Albumin (BSA) as foulant to investigate the antifouling properties of mineralized membranes.

154 The Influence of Surface Morphology on the Performance of Reverse Osmosis Membrane from the Perspective of Water Reclamation.

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In Situ Modification of Desalination Membranes for Improved Performance.

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Nanofiltration (NF) and reverse osmosis (RO) are widely used today for desalination and water treatment. In these membranes nanoscale defects and non-uniformities of the top polyamide layer may reduce overall selectivity. This study examines "caulking" such defects via concentration polarization-enhanced graft-polymerization and tuning selectivity - by filtering the solution of appropriate monomers and initiators through the membrane.[1,2] A novel improvement of this technique reported here is based on addition of a surfactant to the reactive solution, which appears to enhance polarization (via solubilisation of monomer in surfactant micelles) and adherence of graft-polymer to the membrane surface, which facilitates grafting and reduces monomer consumption.

The effect was particularly notable for a hydrophobic monomer glycidyl methacrylate (GMA) combined with a non-ionic surfactant. Surface characterization by ATR-FTIR, HR-SEM and contact angle indicated a significantly increased degree of grafting and uniformity of the coating, compared to a procedure with no surfactant added. Modified ESPA1-2521 elements had permeability comparable to commercial BWRO elements with enhanced rejection of boric acid and representative endocrine-disrupting contaminants (EDCs) compared to their rejection before modification.

The procedure was however less suitable for grafting hydrophilic zwitter-ionic polymers, which has the potential to improve resistance to fouling. For grafting of a zwitter-ionic polymer along with GMA for imparting membrane with both selectivity and antifouling properties, we are currently exploring a two-step procedure whereby GMA with added surfactant is grafted first and zwitter-ionic polymer is added on top of the poly-GMA. Tests of performance, fouling with humic acid, and surface characterization of modified membranes are underway and will be reported.

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155 Comparative Study of NF/RO Membranes for Sustainable Desalination of Produced Water and Frac Flowback Wastewater Following Biological Pretreatment.

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Graphene Oxide Nanocomposite Membranes for High Flux Water Desalination.

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Among various desalination methods, reverse osmosis (RO) technology attracts great interest and has been widely applied due to its lower energy consumption. Further increasing water flux while maintaining high salt rejection would further reduce RO energy consumption. Therefore, developing novel methods to increase water flux through desalination membranes is one of the main research focuses. In this study, graphene oxide (GO) and modified GO were used as a novel additive to the thin film composite (TFC) membranes to significantly increase water flux. Permeability of TFC membrane was greatly enhanced by introducing modified-GO in interfacial polymerization reaction, resulting from the improved hydrophilicity and smoother surface. The achieved water flux of the modified TFC membranes in the best condition was around three times higher than that of the pristine TFC membrane with negligible

influence on salt rejection. GO modified TFC membranes are expected to have great potential for high flux water desalination.

The Impact of Slickwater Fracturing Fluid Composition / Chemical Interactions on Membrane Fouling of Flowback Water.

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Although there is broad interest in the development of membrane systems for treatment of flowback water from natural gas production, there is currently little information on the critical components governing the fouling behavior of these complex fluids. Synthetic flowback water was generated by subjecting mixtures containing friction reducer, breaker, crosslinker and surfactants to the high pressures and temperatures associated with fracking operations in a 1 L Parr reactor that contained pulverized shale outcrops. Dead-end filtration experiments were performed to evaluate the impact of fluid composition and fracturing conditions on the fouling characteristics of flowback water during microfiltration (MF). Polyacrylamide (PAM) based friction reducer (FR) was found to be the most significant membrane foulant. Dynamic light scattering results suggested that the presence of breaker (ammonium persulfate) reduced the mean hydrodynamic diameter of PAM from more than 500 to 80 nm after activation with sodium tetraborate pentahydrate at high temperatures (80). This decrease in size led to a significant reduction in fouling during MF. The adsorption of organic additives within the shale formation during treatment in the Parr reactor was enhanced at high pressures (1200 psi), further reducing fouling by the recovered water. The addition of surfactants to the fracturing fluid led to the formation of a stable emulsion, which eliminated almost all of the fouling during subsequent MF treatment. These results demonstrate the significant interactions between various components used in hydraulic fracturing operations and its impact on membrane fouling, providing valuable suggestions on the development of efficient treatment strategies for flowback waters.

156 A Fouling Comparison Study of Algal, Bacterial, and Humic Organic Matters in Seawater Desalination Pretreatment Using UF Ceramic Membranes.

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WDRC, KAUST, JEDDAH, Saudi Arabia

157 Fouling Behaviour of Forward Osmosis TFC Membranes during Wastewater Reclamation Using Feed Streams Mimicking Treated Effluent.

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158 Process Optimization on Clean Water Recovery from Real Reactive Dyeing Effluents.

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160 Recovery and Reuse of Reactive Dyeing Wastewater By Ultrafiltration.

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162 Sustainable Antibiofouling Properties of Thin Film Composite Forward Osmosis Membrane with Rechargeable Silver Nanoparticles Loading.

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Silver Modified PI Membrane with Enhanced Antifouling Properties.

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To improve antifouling and antibacterial properties of the polyimide (PI) membrane, silver particles are grafted on the membrane surface via a three-step modification route. The reaction mechanism is confirmed by Fourier Transform infra-red analysis (FTIR) and physical characterizations of the modified PI membranes. The anti-biofouling performance is evaluated by disk diffusion test and bacterial suspension immersion experiment. The antifouling effect of the silver-modified membranes is also assessed in the bovine serum albumin (BSA) aqueous solution. Both the anti-biofouling and antifouling properties of the membrane are greatly improved by the silver modification. Effects of the thermal treatment temperature on the property and silver stability of modified PI membrane are also investigated systematically.

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Second Interfacial Polymerization of Thin-Film Composite Polyamide Membrane with Polyethyleneimine for Forward Osmosis Applications.

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Mass Balance Simulation of a Full-Scale Forward Osmosis-Nanofiltration Hybrid System.

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Novel Thin Film Composite Forward Osmosis Membrane with Improved Water Flux and Anti-Fouling Performance with Incorporation of N-[3-(trimethoxysilyl) Propyl] Ethylenediamine (NPED) Amine Monomer.

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In this work, novel thin film composite (TFC) forward osmosis (FO) membranes are developed via interfacial polymerization on the polyacrylonitrile (PAN) substrate, using an organic-inorganic hybrid compound — N-[3-(trimethoxysilyl) propyl] ethylenediamine (NPED) as the amine monomer to mix with m-phenylenediamine (MPD). The PAN substrate was modified with sodium hydroxide and optimized by varying the hydrolyzation time. With the incorporation of NPED in the selective layer, the formed TFC membrane exhibits better hydrophilicity, improved water flux and fouling resistance, and therefore superior membrane performance. By varying the NPED content in the aqueous phase, the surface properties and performance of TFC membranes are investigated with various characterizations. In addition, the anti-fouling properties of the TFC membranes with different NPED content in the aqueous monomer is also studied.

Designing Anti-Oil-Fouling Membrane for Membrane Distillation: Learning from Natural Oleophobic Surfaces and Beyond.

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Membrane distillation (MD) is an emerging, thermally driven, desalination technology using micro-porous hydrophobic membranes. MD has a tremendous potential to become an economically competitive process for desalinating highly saline brine solution (such as shale gas wastewater, which reverse osmosis cannot treat), especially when low-grade thermal energy such as waste heat and geothermal energy is readily available. However, the reliance of MD on the usage of hydrophobic membrane limits its application to treating relatively “clean” saline water that is free of hydrophobic contaminants, as the strong attractive interaction between the hydrophobic contaminants and the hydrophobic membrane would lead to rapid membrane fouling and flux decline. To address the fouling problem in MD, we develop composite MD membranes with oleophobic surface coating inspired by natural surface with anti-fouling properties. Compared to a pristine hydrophobic membrane, the composite membrane showed a significantly more robust MD performance when challenged with a feed solution of oil-water emulsion. Beyond mimicking natural oleophobic surfaces in engineering surface wetting property, we further investigated the impact of other surface properties, such as surface charges, on the anti-oil-fouling performance of the MD membranes. We also conducted time-dependent contact angle measurements and oil-droplet-probe force spectroscopy to unravel the mechanism of oil-adhesion for corroborating the observations regarding membrane fouling in the MD experiments.

166 Modified Microporous Polypropylene Flat Sheet Membrane Via Thermally Induced Phase Separation for Membrane Distillation.

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168 Development of Anti-Fouling, Anti-Microbial Membranes for Wastewater Treatment.

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MEXSY MemBrain in Water Treatment.

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MetaExpert Systems (MEXSY) – is a new class of expert systems for universal applications [1-2]. MEXSY MemBrain project studing MEXSY solutions in the field of membrane science and technology [3] is moving to real applications. So it's necessary to discuss the actual MEXSY MemBrain knowledge base content with professional community (North American Membrane Society).

This presentation considers MEXSY MemBrain knowledge base in whole and in part of water treatment [4] to develop related part of MEXSY MemBrain TechnOntology knowledge portal [1]. For another examples see [5-7].

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169 Highly Permeable Artificial Water Channel in Block Copolymer Membranes.

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Commercial Nanofiber Nonwoven As a Support for Thin Film Composite Membrane for Forward Osmosis.

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Product scale-up for any new emerging technology is key to seeing that technology succeed. Forward osmosis (FO) is one such technology that has been struggling to be a commercially viable technology. A major impediment to this is associated with the challenges that are there due to membrane manufacturing. Those companies that have seen some success with FO scale-up have developed FO membranes that resemble conventional RO membranes, though having certain chemical or structural differences. Many of the highly novel membranes, such as those widely discussed in the academic literature, will likely never see commercial reality because of the challenges associated with making those membranes in large quantity. Electrospun nanofiber supported thin film composite membranes are generally thought to belong to this group. Nanofibers have the properties sought after in FO TFC membrane support materials (high porosity, low tortuosity), and these membranes have shown great promise in the academic literature. However, the production of nanofiber mats at scale has been criticized. Only recently has industrial scale production of nanofibers from companies like DuPont, Donaldson, and Hollingsworth & Vose brought nanofiber membranes into the commercial space. In this work, we demonstrate the use of a commercial nanofiber nonwoven based support media to manufacture thin film composite (TFC) membranes for forward osmosis. We evaluate the viability of this material by comparing it to laboratory grade nanofiber based TFC membranes and commercially available solution casted TFC membranes. The fiber diameter of the nanofiber mat ranges from 445± 135 µm. ATR-FTIR spectrum confirms the successful formation of a polyamide selective layer by in-situ polymerization process and SEM imaging demonstrates the uniformity of the polyamide layer. The TFC membrane has a very high Young's modulus, equivalent tensile strength, and low ductility as compared to a laboratory grade nanofiber based TFC membrane. The TFC membrane generates two times more water flux and ten times less reverse solute flux as compared to a commercial HTI solution cast TFC membrane. These results prove that the commercial nanofiber support is capable of producing better membranes than commercial HTI TFC membrane while maintaining similar standards as the laboratory grade nanofiber supported TFC membrane.

171 Modeling Nanofiltration: The Fundamentals and Its Application in Softening and Pretreatment.

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Effect of Feed Spacer Thickness on the Fouling Behavior in Reverse Osmosis Process - a Pilot Scale Study.

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The performance deterioration of RO membrane processes caused by the accumulation of rejected solutes on membrane surface is an inevitable phenomenon in membrane processes. The feed spacer in spiral wound reverse osmosis (RO) membrane modules can provide the structural support to keep feed channel open and also allow turbulent flow to mitigate solute concentration build-up at the vicinity of membrane surface. The objective of this studywas to investigate the effect of feed spacer thickness on both membrane fouling behavior and cleaning efficiency in a pilot test during a 659 h operation. Furthermore, fouling load distribution was studied by measuring normalized differential pressure of individual elements in pressure vessels. Foulant analysis according to feed spacer thickness was also conducted to compare fouling propensities. This study showed that a thicker feed spacer could reduce membrane fouling and subsequently decrease membrane cleaning frequency and allow an even fouling load distribution along the modules installed in a pressure vessel.

172 Investigation of Environmentally Friendly Solvents for Casting of Water Treatment Membranes.

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Functionalized Cellulose Nanofiber Membranes for Water Purification.

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In this project, high-performance, nanofiber-based ion-exchange membranes were prepared for removal of heavy metals from impaired waters. Our hypothesis was that such membranes would have high metal ion capacities resulting from large surface area-to-volume ratios and high water permeability relative to barrier-type membranes such as reverse osmosis and nanofiltration. The nanofiber membranes were produced by electrospinning cellulose acetate nanofiber mats, which were strengthened by thermal-mechanical annealing and then converted to regenerated cellulose nanofiber mats. Subsequent surface modification transformed the membranes into ion-exchange membranes for removal of trace metal ions in water.

Cellulose acetate was selected as the starting material because it has been used widely to electrospin fibers due to simple processing. The electrospinning formulation and conditions yielded fiber mats having a fiber diameter in submicron range and a thickness range of 160 to 330 μm. Following annealing, the nanofiber mats were converted to regenerated cellulose, which is a low-fouling material that can be modified using convenient surface chemistry to introduce the ion-exchange ligands.

Ion exchange using carboxylate anion ligands is a potential strategy to capture cadmium and nickel ions found in industrial wastewaters. Thus, the regenerated cellulose nanofiber mats were modified by grafting poly(itaconic acid) (dicarboxylic acid side groups) and poly(acrylic acid) (monocarboxylic acid side groups) to the surfaces of individual nanofibers that had been modified with poly(glycidyl methacrylate).The success of poly(itaconic acid) and poly(acrylic acid) grafting was confirmed by attenuated total reflectance Fourier-transform infrared spectroscopy.

Direct-flow filtration measurements showed that the nanofiber membranes have water permeabilities of 400-1600 L/m^2/bar/h, much higher than reverse osmosis or nanofiltration membranes. The single-component ion-exchange isotherms were measured at constant pH for cadmium, nickel, and calcium ions. Competitive sorption measurements were made using environmentally relevant concentrations of these ions to determine the selectivity of the membranes for cadmium ions. Experimental isotherms for Cd-Ca and Cd-Ni were compared to model predictions. The multi-component isotherms for Cd-Ca and Cd-Ni systems were modeled using the competitive Langmuir model with Langmuir parameters obtained by fitting single-component isotherms.

Results show that the polymer-modified nanofiber membranes have outstanding permeability and high selectivity for heavy metals over a common competing anion present at much higher concentration. The nanofiber membrane adsorbers bind cadmium ions with static capacities that are similar to and, in some cases, superior to commercial ion-exchange resins and activated carbon.

173 Advancements in Switchable Polarity Solvent Forward Osmosis (SPS FO) Water Treatment Technology.

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Development of Novel Low-Fouling RO Membrane.

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Membrane fouling is one of the most significant problems for the stable operation of reverse osmosis (RO) membranes. To improve low-fouling property of RO membranes, a study of membrane surface was carried out. With the control of hydrated water on membrane surface, a new membrane performed adhesion inhibition of various foulant, such as non-ionic surfactant, anionic surfactant, and cationic surfactant. In cooperation with Toray Singapore Water Research Center, the remarkable reduction of foulants on the membrane surface was observed through optical coherence tomography analysis, and the new membrane performed a superior flux retention than a conventional membrane under a secondary treated sewage.

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The Water Flux Properties of Negative and Positive Electric Charged Monodisperse Particles Using Water Treatment Membrane.

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Exploring Water Reuse with a Novel FO-DCMD Hybrid Membrane Process.

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Optimizing Design Parameters for Thin Film Composite Hollow Fiber Membranes and Module for Forward Osmosis.

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Numerical Analysis and Experimental Investigation of Nano-Composite Ultrafiltration Membranes for Water Treatment.

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Nanocomposite membranes have been used as a promising technology in water treatment. A variety of nanoparticles have been reported to increase the membrane permeability, selectivity and antifouling properties. Nanoparticles with different physicochemical properties have different effects on the membrane structural and operational behavior. There is a need of predicting nanocomposite membranes for design and optimization purposes to control the membrane flux, fouling, module position and to consider energy consumption. A three-dimensional computational fluid dynamics (CFD) model was used to simulate cross-flow membrane process and fluid flow by solving Navier-Stocks equations coupled with the Darcy's law. Nanocomposite membrane flux was modeled at different cross-flow velocity and different operational pressure. Also, effect of membrane structural properties such as porosity and thickness was studied. This CFD model can be used to better apprehend fluid flows in different geometries and to test the impact of operational parameters on nanocomposite membranes flux and finally could help to effectively increase the permeate flux, reduce the fouling on the membrane. The modeling data is validated with experimental data regarding to nanocomposite membrane flux.

Development of Thin Film Composite Polyamide Membranes with Polydopamine/Molecular Sieve Layers for Water Desalination through Reverse Osmosis.

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We developed a method to increase membrane performance and particle stability of molecular sieves in traditional polyamide thin film nanocomposite (TFN) membranes. Compared to common particle addition into polyamide casting solution, we stabilized particles by thin bio-inspired adhesion polydopamine layer, on microporous polysulfone support, and then we interfacially synthesized polyamide on top of this layer. In this work, we present our results for development of thin film composite (TFC) polyamide membranes on polydopamine layer with molecular sieves particles on polysulfone support membrane. First, we synthesized dopamine layer with different particle content and different particle size. Then, we synthesized a series of polyamide membranes via interfacial polymerization. For comparison, we also synthesized regular TFC and TFN polyamide membranes. Then we measured the permeability and selectivity performance

using dead-end filtration and cross-flow testing system. We report the synthesized membrane surface and morphology result with contact angle, Fourier transform infrared spectroscopy, scanning electron microscopy, and atomic force microscopy.

The Impact of Slickwater Fracturing Fluid Composition / Shale Interactions on Membrane Fouling of Flowback Water.

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Although there is broad interest in the development of membrane systems for treatment of flowback water from natural gas production, there is currently little information on the critical components governing the fouling behavior of these complex fluids. Synthetic flowback water was generated by subjecting mixtures containing friction reducer, breaker, crosslinker and surfactants to the high pressures and temperatures associated with fracking operations in a 1 L Parr reactor that contained pulverized shale outcrops. Dead-end filtration experiments were performed to evaluate the impact of fluid composition and fracturing conditions on the fouling characteristics of flowback water during microfiltration (MF). Polyacrylamide (PAM) based friction reducer (FR) was found to be the most significant membrane foulant. Dynamic light scattering results suggested that the presence of breaker (ammonium persulfate) reduced the mean hydrodynamic diameter of PAM from more than 500 to 80 nm after activation with sodium tetraborate pentahydrate at high temperatures (80). This decrease in size led to a significant reduction in fouling during MF. The adsorption of organic additives within the shale formation during treatment in the Parr reactor was enhanced at high pressures (1200 psi), further reducing fouling by the recovered water. The addition of surfactants to the fracturing fluid led to the formation of a stable emulsion, which eliminated almost all of the fouling during subsequent MF treatment. These results demonstrate the significant interactions between various components used in hydraulic fracturing operations and its impact on membrane fouling, providing valuable suggestions on the development of efficient treatment strategies for flowback waters.

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Fabrication and Characterizations of Hollow Fiber Membranes for Removing Virus and Bacteria.

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179 The Validation of a Stepwise Model of Direct Contact Membrane Distillation for Large-Scale Applications.

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POSTER PRESENTATION III- GAS AND MOLECULAR SEPARATION

Carbon Molecular Sieve Membranes for Mixed Olefins-Paraffins Separations.

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Light olefins, such as ethylene (C_2H_4) and propylene (C_3H_6), are key building blocks for the petrochemical industry. The separation of olefins from paraffins is typically carried out by energy-intensive distillation. It is, therefore, appealing to develop olefins-selective membranes for use in a hybrid membrane-distillation process to retrofit the current distillation separation processes to lower the overall energy usage.

Carbon molecular sieve (CMS) membranes are able to exceed the limitation of the trade-off between productivity and efficiency of traditional polymeric membranes. In this work, starting materials and processing conditions were investigated in order to explore the impact on CMS membranes separation properties for mixed olefins/paraffins. CMS membranes were made having useful olefins/paraffins separation performance, which will be reported.

Physical Aging of Perfluoropolymers in Ultrathin Film Composite Membranes.

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Thin film composite (TFC) membranes for gas separation are comprised of a selective layer of glass polymers, which are usually subjected to physical aging, i.e. permeability decreases with time. The aging behavior has been ascribed to the rearrangement of polymer chains in the thin film, resulting in changes in free volume (f) and glass transition temperature (T_g). Our objective is to investigate the effect of physical aging on gas permeance, selectivity and T_g of the selective layer in the TFC membranes. Two-layer TFC membranes consisting of perfluoropolymers of Teflon® AF or Hyflon® AD at various film thicknesses (50 – 400 nm) on polyethersulfone ultrafiltration support were prepared. Pure-gas permeances of CH_4, N_2, H_2 and CO_2 at 35 °C were measured and monitored for aging over 1000 hr. Apparent T_g of the thin selective layer was measured over time by a new thermo-mechanical method, Nano Thermal Analysis. In general, aging decreases gas permeances and increases T_g, and the rate of changes is more significant for thinner films. For example, after aging for 2000 hr, N_2 permeance decreases from 1000 gpu to 550 gpu by 45% and T_g increases from 160 °C to 172 °C in a TFC membrane with 100-nm thick Teflon® AF1600. In this talk, we will compare the aging behavior and gas permeance reduction of the TFC membranes with those of freestanding thin films. More importantly, for the first time we have developed a correlation between the gas permeance reduction and T_g increase using the free volume model to explain the physical aging behavior.

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Polyamide Thin-Film Composite Membranes for Potential Raw Biogas Purification: Experiments, Modelling and Scale-up.

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Colloidal ZIF-8 PBI/6FDA-DAM Immiscible Polymer Blend Membranes for H2/CO2 Separation.

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Colloidal ZIF-8 PBI/6FDA-DAM Immiscible Polymer Blend Membranes for H_2/CO_2 Separation

Yu Huang, Nimanka P. Panapitiya, Edson V. Perez, John P. Ferraris, Kenneth J. Balkus, Jr., Inga H. Musselman

ABSTRACT

High pressure and high temperature separation of H_2/CO_2 is of great interest for clean energy generation in processes such as coal gasification. Flat and tubular membranes of the polybenzimidazole (PBI)/6FDA-DAM immiscible blend containing colloidal ZIF-8 were prepared to test the gas separation performance of single gases and the H_2/CO_2 gas mixture at various pressures and temperatures. It was found that the amount of colloidal ZIF-8 in the blend has a remarkable effect on membrane morphology and gas separation. An increase of the loading for the colloidal ZIF-8 in the blend leads to a decrease in the size for the dispersed 6FDA-DAM domains. A higher experimental temperature resulted in higher gas permeance through the membrane, while the gas selectivity remained constant. At 30 atm and 300 °C, a 5% colloidal ZIF-8 PBI/6FDA-DAM membrane exhibited a H_2 permeance of 29.74 GPU (approximately 476 Barrer), an ideal H_2/CO_2 selectivity of 16.1, and a H_2/CO_2 gas mixture selectivity of 11.4. In comparison to other membranes, this polymer blend membrane shows high gas permeance and high gas selectivity, and it surpasses the upper bound of the 2008 Robeson plot for H_2/CO_2.

Membrane Separation of CO2 from Syngas Using PDMS and Mixed Matrix Membranes.

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Membrane Separation of CO_2 from Syngas Using PDMS and Mixed Matrix Membranes

Carbon dioxide (CO_2), being one of the leading global greenhouse gas emissions, can be important to remove from other gaseous components in downstream processing. In processes such as gasification or dry CH_4 reforming, CO_2 along with syngas (CO and H_2) are the primary products. In order for syngas to be used in other processes, such conversion into methanol or ammonia, these components must be separated. Polymeric membranes have been proven to selectively separate CO_2 over syngas, due to the favoured transport mechanism. Along with these materials, mixed matrix membranes are also proving to be novelty separation methods, combining the adsorption and membrane separation mechanisms to further improve their performances. In this study, commercial pure PDMS membranes, along with PDMS mixed matrix membranes including activated carbon and zeolites were investigated for CO_2 removal from syngas.

Mixed Matrix Membrane Development for CO2 Capture.

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Mixed matrix membranes (MMM) have the potential to achieve high performance to capture CO_2 from flue gas. The most difficult challenge is fabricating defect free and optimized MMMs. Defects are generally due to incompatible interfaces between the polymer and the filler particle. Here, we present the fabrication of defect-free MMM by engineering the polymers and metal organic frameworks. Thermal, mechanical and gas transport properties confirmed the improved interaction between the polymer and the MOFs. Also, an attempt was made to fundametally understand the gas transport through the MMMs. MMMs showed significantly enhanced CO_2 permeability and CO_2/N_2 selectivity compared to the pure polymer membranes. These results confirm the success of the proposed technique to mitigate defective Polymer/MOF interfaces. The potential polymers and MMMs were coated on the porous hollow fibers supports using dip coating technique and gas separation performance testing of these thin membranes under flue gas conditions showed the stable CO_2 permeability and CO_2/N_2 selectivity.

184 Modeling Gas Sorption in Thermally Rearranged Polymers:.

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Bulky Diamines Modified Crosslinkable Polyimides Hollow Fiber Membranes for Natural Gas Purification.

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6FDA-based polyimide membranes have received particular attention in natural gas separation. Covalent ester crosslinking is considered as an effective approach to stabilize the membranes against CO_2 plasticization. In the past, it was found that during the crosslinking, collapse of the thin transition layer of asymmetric hollow fibers can occur, thereby causing large losses in permeance. The current work explores partial replacement $-CH_3$ groups of PDMC (propanediol monoester crosslinkable 6FDA-DAM:DABA 3:2

polyimide) by more bulky –CF_3 groups to inhibit the transition layer collapse responsible for loss in permeance of the standard PDMC fibers during crosslinking. It was found that the introduction of bulky and rigid diamine increases the β-transition temperature of PDMC by increasing the rotational barrier for side group mobility. Low molar fractions (5%) of CF_3-diamine modified PDMC polymer was synthesized and engineered to defect-free hollow fiber membranes by optimizing the dope composition and spinning conditions. The crosslinked PDMC-CF_3 asymmetric hollow fiber membranes, without sacrifice of permeance, exhibited an excellent CO_2 separation performance under aggressive feeds (high pressure, impurities of hydrocarbons), showing great potential in natural gas purification.

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Synthesis and Characterization of Tetraamino Diphenyl Sulfone (TADPS) Based Polybenzimidazoles and Post-Modification for Gas Separation Membranes.

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Cellulose Triacetate Doped with Ionic Liquids for CO2/CH4 Separation.

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Polymeric membranes have been widely used for the removal of CO2 from natural gas. It is a leading technology for offshore platform applications and is gaining more competitive advantages over conventional amine absorption for onshore applications. The work horse membrane material for industrial CO2/CH4 separation is cellulose acetate/triacetate (CTA). The more widely use of CTA is, however, limited by its high crystallinity, leading to low CO_2 permeability. The goal of this work is to reduce the crystallinity in CTA by doping with ionic liquids such as [emim](BF_4) and [emim](DCA), to improve the CO2/CH4 separation properties. Both ionic liquids have CO_2/CH_4 solubility selectivity higher than CTA. In this project, we have prepared series of CTAs doped with various contents of [emim](BF_4) or [emim](DCA). The effect of ionic liquids on the crystal formation in CTAs was characterized using DSC and

WAXD. Doping of ionic liquids can reduce or completely inhibit the crystal formation in CTA, resulting in an increase in gas solubility and permeability. The presentation will discuss the effect of the doping of ionic liquids on the physical properties of the blends, including morphology and pure-gas solubility, diffusivity and permeability. The blends exhibit the highest CO2/CH4 solubility selectivity among the polymers known. The addition of ILs also moves the separation performance towards the upper bound, which makes them interesting platform for CO2/CH4 separation.

Membrane Process Optimization for Carbon Capture.

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Concerns over the effects of anthropogenic carbon dioxide (CO2) emissions from fossil-fuel electric power plants has led to significant efforts in the development of processes for CO2 capture from flue gas. Options under consideration include absorption, adsorption, membrane, and hybrid processes.

The US Department of Energy (DOE) has set goals of 90% CO2 capture at 95% purity followed by compression to 140 bar for transport and storage. Ideally, the levelized cost of electricity (LCOE) would increase by no more than 35%.

Membrane Technology and Research, Inc. (MTR) has proposed a promising design that combines membrane capture with cryogenic condensation [JMS 359 (2010) 126-239]. The process utilizes a two-stage membrane process in which the feed air to the furnace sweeps the flue gas in the second stage to reduce the flow of CO2 in the effluent to 10% of that leaving the furnace. Such a design significantly reduces capture costs but leads to a detrimental reduction in the oxygen concentration of the feed air to the boiler.

The transport properties and operating pressures of the membrane stages are optimized in this study. Membrane selectivity is varied over a broad range encompassing the values considered by MTR. Permeability is varied with selectivity according to the variation anticipated by the upper bound of the Robeson plot for CO2 and nitrogen. Membrane permeance is calculated assuming membranes can be fabricated with an effective thickness of 0.1 micron. Additionally the two stages may utilize different membrane materials. The feed and permeate pressures also are varied over ranges encompassing the values proposed by MTR.

The optimization space of membrane properties and operating conditions is scanned globally to determine the process design that minimizes LCOE. The oxygen concentration to the boiler is evaluated during the optimization process and can be used to constrain viable alternatives. The results indicate a fairly broad range of membrane properties can yield comparable LCOE near the minimum. The optimal operating pressure range is somewhat narrower. The minimum allowable oxygen concentration can constrain viable designs significantly and is critical to process economics.

Towards a Truly Hybrid Membrane for Organic Solvent Filtration.

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MEXSY MemBrain at Stanford, Exaple: Membrane Gas Separation.

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MetaExpert Systems (MEXSY) – is a new class of expert systems for universal applications [1-2]. MEXSY MemBrain project studing MEXSY solutions in the field of membrane science and technology [3] is moving to real applications. So it's necessary to discuss the actual MEXSY MemBrain knowledge base content with professional community (North American Membrane Society).

This presentation considers MEXSY MemBrain knowledge base in whole (membrane science and technology) and in part of membrane gas separation, carbon capture, and some other problems studing at Stanford University [4-5] to set connection between MEXSY MemBrain project (developing since 1999) and MEXSY StanfordBrain project (developing since 2012). Two parts of StanfordBrain (universal knowledge base of Stanford University), the LabBrain (laboratories, centers, projects, publications, etc) and the OntoEducation (schools, departments, programs, courses, etc), need to connect with MEXSY MemBrain. First of all, to connect with Stanford related part of the MEXSY MemBrain knowledge base. Then the experience of LabBrain and OntoEducation connections will transfer to another parts of the MEXSY MemBrain system (Membraine Characterization, Water Treatment, Fuel Cells [6], etc).

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High Temperature and High Pressure Gas Separation Properties of Polybenzimidazole Membranes Dried at Different Temperatures.

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Polybenzimidazole (PBI) membranes are mechanically and chemically resilient making them suitable for the separation of gases at high pressure and high temperature. Hydrogen/carbon dioxide gas selectivities ranging from 5 to 24 have been reported for PBI membranes measured at temperatures up to 250 °C, illustrating significant temperature-dependent permselectivity properties. We investigated the effect of drying temperature and testing conditions on the gas permeation properties of PBI membranes. Four sets of PBI membranes were cast and then subjected to a final drying temperature of 250, 300, 350, or 400 °C. The gas separation properties of the membranes dried at 250 °C and at 300 °C were measured at 35, 100, 200, and 300 °C with upstream pressures of 5, 15, 30, and 45 atm. The PBI membranes measured at 35 °C exhibited H_2/CO_2 selectivities that ranged from 18 to 50 when tested with pure gases and up to 72 when tested with gas mixtures over the pressure range studied. PBI membranes dried at 250 °C and tested at 35 °C demonstrated H_2/CO_2 ideal selectivities that ranged from 18 at 5 atm to 33 at 30 atm. When the same membranes were tested at 300 °C, the H_2/CO_2 ideal selectivity remained almost unchanged (28 at 5 atm and 30 at 30 atm). Membranes dried at 300 °C exhibited improved separation properties when tested at 35 °C, showing a H_2/CO_2 ideal selectivity of 49 at 5 atm, 53 at 30 atm, and 47 at 45 atm. Using a gas mixture, the H_2/CO_2 selectivity at 35 °C and 30 atm was even higher at 72. These results suggest that PBI membranes need to be dried at high temperatures to fully maximize their separation properties.

Field Trials of Spiral-Wound Proteus Membrane Modules for H2/CO2 Separation from Shifted Coal-Derived Syngas.

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A membrane test skid designed to treat 50 pounds per hour of coal-derived syngas has been installed and operated at the Power Systems Development Facility (PSDF) located at the National Carbon Capture Center (NCCC) in Wilsonville, Alabama, USA. This membrane system has been used for several 500 to 1000-hour long operating campaigns to evaluate the separation performance and stability of the hydrogen-selective Proteus membrane developed by MTR. Syngas from the air-blown PSDF gasifier is subjected to a water-gas-shift prior to being delivered to the membrane skid at 12 barg and ambient temperature with a typical (dry-basis) composition of 70% N_2, 12% CO_2, 12% H_2, 3% CO and balance CH_4. The H_2S content of the feed stream ranges from 100-400 ppm. The skid is equipped to heat the syngas feed and operate membrane modules continuously at elevated temperatures (100-140ºC). This work summarizes the results from Proteus field test campaigns that were completed during the past year at the NCCC. Parametric tests performed on bench-scale (2.5-inch diameter) Proteus modules at 120ºC revealed a strong dependence of module H_2 permeance and H_2/CO_2 selectivity on feed flowrate. Enhancement in module H_2 permeance was observed with increased temperature from 100 to 135ºC, with little change in H_2/CO_2 selectivity. Furthermore, full-length 4-inch diameter modules operated at 120ºC for the entirety of the campaign (~600 hours) showed stable performance and excellent selectivity (H_2/CO_2 = 15-20).

Highly-Efficiently Enhancing PEO Membrane Properties Toward Sustainable CO2 Separations.

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Herein, we first report an extremely versatile strategy to significantly improve gas transport properties of PEO-containing cross-linked membranes based on their specific swelling properties. Low-molecular-weight poly (ethylene glycol) (PEG) was deliberately incorporated into synthesized swellable pure PEO cross-linked membrane via immersing PEO membrane into PEG-water solution and membranes with various PEG loadings are obtained. The imbedded PEG molecules can be located between polymer chains to improve chain mobility and increase chain distance, resulting in the increase of fractional free volume (FFV), which is in favor of gas diffusion. On the other hand, the increment of CO_2-philic building units resulting from the imbedded PEG molecules leads to higher CO_2 solubility. Finally, the simple treated membranes exhibit significant increments in both CO_2 permeability (up to 762%) and CO_2/H_2 selectivity (up to 86%). The separation performance was correlated nicely with the microstructure of the membranes. This study may provide useful insights about the formation and mass transport behaviour of highly-efficient polymeric membrane applicable to clean energy purification and CO_2 capture, and possibly bridge the material-induced technology gap between academia and industry. Most importantly, our discovered strategy has great potential for treating composite membranes and regenerating “aged” membranes to realize clean energy purification and CO_2 capture by membrane technology.

Novel Thermally Cross-Linked Polyimide Membranes for Ethanol Dehydration Via Pervaporation.

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In this work, two novel carboxyl-containing polyimides, 2,2′-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride-4,4′-diaminodiphenylmethane/3,5-diaminobenzoic acid (6FDA-MDA/DABA, FMD) and 3,3′,4,4′-benzophenone tetracarboxylic dianhydride-4,4′-diaminodiphenylmethane/3,5-diaminobenzoic acid (BTDA-MDA/DABA, BMD), are synthesized via chemical and thermal imidization methods, respectively, and employed as pervaporation membranes for ethanol dehydration. Chemical structures of the two polyimides are examined by FTIR and TGA to confirm the successful synthesis. A post thermal treatment of the polyimide membranes with the temperature range of 250 to 400 °C is applied, and its effects on the membrane morphology and separation performance are studied and characterized by FTIR, TGA, WXRD, solubility and sorption test. It is believed that the thermal treatment of the carboxyl-containing polyimide membrane at a relative low temperature only leads to the physical annealing, while it may cause the decarboxylation-induced cross-linking at a higher temperature. In addition, the operation temperature in pervaporation is also varied and shown to be an important factor to affect the final membrane performance. Performance benchmarking shows that the developed polyimide membranes both have superior pervaporation performance to most other flat-sheet dense membranes. This work is believed to shed useful insights on polyimide membranes for pervaporation applications.

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CO_2-Selective Membranes Containing Sterically Hindered Polyvinylamine.

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Light-Responsive Membranes for Gas Separation.

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Recent developments in the field of coordinated porous materials (including metal organic frameworks and zeolitic imidazolate frameworks) have demonstrated that it is possible to tailor CO2 sorbents that respond dynamically to illumination with UV and/or broadband light, such that they cyclically adsorb and desorb CO2 according to the illumination state. This has been achieved via several routes, including through the use of light-responsive ligands, light-responsive guest molecules located within the pores, and via adsorption of a light-responsive dye.

Since the use of these materials as light-responsive sorbents is challenging (due to engineering constraints in providing unhindered gas and light access to as much of the sorbent as possible), it is highly desirable to incorporate them into thin polymeric membranes to create mixed-matrix membranes with light responsive properties. This could lead to membranes with switchable separation characteristics, or other desirable properties such as some form of self-cleaning or self-regeneration after pore blocking.

This presentation will unveil the recent developments in our lab as we develop these novel mixed-matrix membrane materials, including an overview of the light-responsive porous materials we have synthesised and characterised, the design and performance of our newest illuminated test cells for both flat sheet and hollow-fibre membranes (using a unique in-situ LED lighting arrangement to provide maximum illumination and simplify gas sealing).

Carbon Molecular Sieve Membranes from Compatibilized Polyimide-Polybenzimidazole Immiscible Polymer Blends for Gas Separations.

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Separation of gases from mixtures is an important industrial process. High gas selectivity of one polymer and high gas permeability of another could be combined by the use of polymer blend membranes to improve gas pair separation. Compatibilization of immiscible polymers must be done in order to further improve the properties of these membranes. Although, better selectivities for gas pairs could be obtained from polymer precursor membranes, the permeability values remain low. Carbonization of the precursor membranes at high temperatures under inert environment is employed to improve the separation properties of these membranes. Especially, high H_2 permeability values are obtained together with high gas pair selectivities, which are two basic requirements for the industrial applications.

189 CFD Numerical Simulations for Gas Separation Membrane Module Designs.

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190 Metallic Membranes and N2 Separation.

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Development of Sorption Controlled Hollow Fiber Membrane for CO2 Separation.

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The object of this study is to develop hollow fiber membrane with high CO_2 sorption property using chemical synthesis and modification method. Novel polyimide based material with excellent permeation property is systhesized using chemical imidazation method. High CO_2 soluble materials such as polyethylene glycol and ionic liquid are used as additive in main polymer for increase of CO_2 selectivity. Flat sheet type high CO_2 permeable polymer was fabricated and measured the gas separation property. And then the hollow fiber membrane is prepared to confirm potential for commercialization. The Ionic liquid mainchain polymer is also developed to investigate the gas permeability and potential for utilization to coating materials of supported membrane. Polyimide with pendant ionic liquid (Im-PpC) membrane showed the high $\alpha(CO_2/N_2)$ value and the main chain polymer prepared by UV crosslinking with PEG & ILMP crosslinker also showed high $\alpha(CO_2/N_2)$, especially, ILM[3:1] polymer has the highest value in the world because of high solubility of PEG moiety.

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ZIF-67 Filled PDMS Mixed Matrix Membranes for Comprising of Recovery of Bio Ethanol Via Pervaporation.

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Sorption Enhanced Mixed Matrix Membranes for H2/CO2 Separation at Elevated Temperature.

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Gas Separation Properties of Unsupported Carbon Molecular Sieve Membranes Obtained from Blends of High Temperature Rigid Aromatic Polymers.

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Carbon molecular sieve membranes (CMSM) is an emerging technology in gas separations that could offer an outstanding relationship of permeability and selectivity for different gas pairs. In the present work, CMSM's from polyimide PI DPPTD-MIMA, polybenzimidazole (PBI) and their blends are reported. CMSM's preparation was performed at a pyrolysis temperature of 600ºC following a method reported by Ning and Koros (2014). Wide angle X-ray diffraction (WAXD) measurements were performed on CMSM using a SIEMENS 5000 X-ray diffractometer with CuKα radiation (wavelength 1.54 Å). Diffraction patterns show an amorphous halo with two maxima d-spacing obtained by Bragg's law ($n\lambda=2d \sin\theta$): the first between 6.17 - 6.37 Å and the second was located on ~4 Å. In CMSM`s obtained from PI DPPTD-MIMA/PBI blends, the intensity of each maxima d-spacing show a variation related with the presence of PBI in membrane precursors. Gas transport properties were determined by a variable-pressure constant-volume method. Gas permeability coefficients were measured at 35ºC and 2 atm upstream pressure for He, O_2, N_2, CH_4 and CO_2. Permeability coefficients follow an order related to gas kinetic diameters ($P_{He} > P_{CO2} > P_{O2} > P_{N2} > P_{CH4}$). Higher permeability coefficient than in the PI DPPTD-MIMA and PBI polymer precursor was obtained for CO_2 (P_{CO2} = 435.79 Barrer) and O_2 (P_{O2} = 118.10 Barrer).CMSM from PI DPPTD-MIMA/PBI surpass separation performance trade-off for various industrial interesting gas pairs, CO_2/CH_4 (selectivity = 56.04) and O_2/N_2 (selectivity = 8.47) separation. It was found that PBI concentration in membrane precursors affects gas separation properties in CMS membranes by diminishing permeability coefficients for all gases tested and selectivity for the gas pairs studied. Gas permeability coefficients temperature dependence in CMS membranes between 35 and 65ºC at 2 atm upstream pressure was examined. The results show that gas permeability coefficients for CMSM membranes increase with temperature following an Arrhenius type behavior.

194 The Investigation of Perfluorocompound Gases Separation with Hollow Fiber Membrane.

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195 The Study of Solid Polymer Electrolyte Composite Hollow Fiber Membrane for Olefin Gas Separation.

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196 Investigation of High Permeable Polyimide Hollow Fiber Membrane for Gas Separation.

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The Polymeric Upper Bound for N2/NF3 Separation and Beyond; ZIF-8 Containing Mixed Matrix Membranes.

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Global production for NF_3 is continuously increasing, especially due to its heavy consumption in the semiconductor industry. Even though the amount of its emission is relatively small compared to other greenhouse gases, especially CO_2, its relatively long atmospheric lifetime makes its emissions cumulative, possibly causing global climate change. Membrane-based separation technique can be an attractive alternative for the energy-efficient NF_3 recovery, and thereby, evaluating the N_2/NF_3 separation performance by using commercial polymeric membranes is crucial. For the first time, the empirical N_2/NF_3 upper bound relationship was established by using a wide variety of commercial polymeric membranes including both glassy and rubbery polymers based on their single gas (i.e., N_2 and NF_3) permeation characterization. Among them, 6FDA-DAM:DABA (3:2), Teflon® AF 2400 and PTMSP were found to show relatively high N_2/NF_3 separation performance. The theoretical N_2/NF_3 upper bound curve was also defined and it was comparable with our empirical upper bound limit. In addition, diverse

zeolitic imidazolate frameworks (i.e., commercial ZIF-8 (Basolite® Z1200), house-made ZIF-8 or ICA-ZIF-8) were incorporated into Matrimid® 5218 as molecular sieves to improve the N_2/NF_3 separation performance. More specifically, the effect of solvent, particle size and ligands on the transport properties in mixed matrix membranes was investigated.

197 Tuning PIM-PI/Z-MOF-Based Mixed-Matrix Membranes for Highly Efficient Propylene/Propane Separation.

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Impact of Humidity on Sulfonyl-Containing Polybenzimidazoles for Gas Separations.

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Due to their high chemical and thermal stability, polybenzimidazoles (PBIs) are promising candidates for use as gas separation membranes for high temperature applications. A series of sulfonyl-containing PBIs based on the 3,3',4,4'-tetraaminodiphenylsulfone (TADPS) monomer were recently synthesized and shown to have enhanced solubilities in common organic solvents relative to commercial PBI (Celazole^{TM}), thus improving their processability. Celazole^{TM} and TADPS-based PBIs show a strongly hydrophilic behavior, and can uptake up to 25% water by mass at room temperature. Due to the potential effects of water uptake on both mechanical and gas transport properties, this study seeks to understand the fundamentals of the interactions between water and PBIs. Water vapor gravimetric sorption and dilation measurements have been performed at 35 °C, and a significant hysteresis was observed during desorption experiments, due to swelling and plasticization. The specific volume of the water-polymer mixture as well as the partial molar volume of water in the glassy polymer have also been calculated. Furthermore, a separate FTIR analysis showed that strong hydrogen-bonding interactions occur between water molecules and the PBI backbone.

Development and Characterization of Hollow Fiber Membrane with High CO2 Selectivity.

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In this study, we prepared the polyimide based hollow fiber membrane with High CO2 permeance property. In other to prepare high permeable gas separation membrane, we synthesized novel polyimide material using 6FDA, Durene and PEG monomers. And then general property of the polyimide membrane is characterized using flat sheet type of membrane. The membranes were prepared under various controlled conditions such as retention time and concentration of the polymer. And then the hollow fiber membrane is also prepared and then characterized for confirmation of their potential. The Ionic liquid mainchain polymer is also developed to investigate the gas permeability and potential for utilization to coating materials of hollow fiber membrane. Polyimide with pendant ionic liquid (Im-PpC) membrane showed the high $\alpha(CO_2/N_2)$ value and the main chain polymer prepared by UV crosslinking with PEG & ILMP crosslinker also showed high $\alpha(CO_2/N_2)$

198 Performance Prediction of a Tubular Membrane Contactor for CO2 Absorption in Reactive Aail-Based Solvent.

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Analysis of the Transport Properties of Thermally Rearranged (TR) Polymers and Polymers of Intrinsic Microporosity (PIM) Relative to Upper Bound Performance.

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The properties of polymers which lie along the upper bound are not necessarily determined purely by diffusion selectivity. For many materials, solubility selectivity helps push these limits, while diffusion selectivity is dominant for select gas pairs. A critical analysis of the comparison of diffusion selectivity, solubility selectivity, diffusivity, and solubility constants has been used to analyze the transport properties of thermally rearranged (TR) polymers and polymers of intrinsic microporosity (PIMs), two types of polymers which consistently preform at or beyond the polymer upper bound for select gas pairs (O_2/N_2 and CO_2/N_2). PIMs and TR polymers have higher diffusion coefficients than glassy polymers with similar size sieving abilities and have high O_2 and CO_2 solubility. Additionally, the previously determined diffusion gas kinetic diameters, d_g, provide the best correlation with diffusion coefficients of PIMs and TR polymers and serve to better analyze transport properties of upper bound materials. Based on this analysis of diffusion and solubility data for PIMs and TR polymers, upper bound performance can be achieved when diffusion selectivity, diffusion coefficients, and gas solubility are all maximized.

Poster-Membrane Process Optimization for Carbon Capture.

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Membrane Process Optimization for Carbon Capture
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University of Toledo

Key Words: carbon dioxide, Post-combustion CO_2 capture, hollow fiber membrane

Concerns over the effects of anthropogenic carbon dioxide (CO_2) emissions from fossil-fuel electric power plants has led to significant efforts in the development of processes for CO_2capture from flue gas. Options under consideration include absorption, adsorption, membrane, and hybrid processes.

The US Department of Energy (DOE) has set goals of 90% CO_2 capture at 95% purity followed by compression to 140 bar for transport and storage. Ideally, the levelized cost of electricity (LCOE) would increase by no more than 35%.

Membrane Technology and Research, Inc. (MTR) has proposed a promising design that combines membrane capture with cryogenic condensation [JMS 359 (2010) 126-239]. The process utilizes a two-stage membrane process in which the feed air to the furnace sweeps the flue gas in the second stage to reduce the flow of CO_2 in the effluent to 10% of that leaving the furnace. Such a design significantly reduces capture costs but leads to a detrimental reduction in the oxygen concentration of the feed air to the boiler.

The transport properties and operating pressures of the membrane stages are optimized in this study. Membrane selectivity is varied over a broad range encompassing the values considered by MTR. Permeability is varied with selectivity according to the variation anticipated by the upper bound of the Robeson plot for CO_2 and nitrogen. Membrane permeance is calculated assuming membranes can be fabricated with an effective thickness of 0.1 micron. Additionally the two stages may utilize different membrane materials. The feed and permeate pressures also are varied over ranges encompassing the values proposed by MTR.

The optimization space of membrane properties and operating conditions is scanned globally to determine the process design that minimizes LCOE. The oxygen concentration to the boiler is evaluated during the optimization process and can be used to constrain viable alternatives. The results indicate a fairly broad range of membrane properties can yield comparable LCOE near the minimum. The optimal operating pressure range is somewhat narrower. The minimum allowable oxygen concentration can constrain viable designs significantly and is critical to process economics.

200 Dual CO2- and N2-Selective Intrinsically Microporous Hydroxyl-Functionalized Triptycene-Based Polyimide for Natural Gas Upgrading.

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POSTER PRESENTATION IV -LIFE SCIENCE, BIOMEDICAL, AND/OR SENSORS

Recovery of Organic Solvents from Vegetable Oil Streams.

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Membrane separation is increasingly used for the processing of organic solvents systems. Apart from targeting at very specific separations, such membranes are suitable for upgrading of solvent recovery. In current industry, a combination of membrane technology and distillation/evaporation is the most relevant.

Currently used distillation/evaporation is expensive (energy) and sometimes introduces degradation of products (lowering quality). Less heat input in the products by using membranes should improve continuous quality at lower costs. But when solvent is recovered with membranes the throughput of the membrane is not constant-due to concentration polarization and fouling. This leads to a point where membranes are less effective. In a constellation of membrane and evaporation this means that there are optimal conditions –for membranes in technical sense and for the process for the overall economics.

We have modeled and experimented a few systems to explore the optimal regimes. In this area membrane permeation and separation as well as ease of evaporation and energy costs play a role. Solsep has also experimented with systems that can handle high viscosity feeds and promise relatively high and well-defined mass-transfer properties. This could shift the optimal point to less evaporation. For eg acetone-veggy oil streams it has been found that membranes can be extremely attractive giving well-defined product quality with decreased costs. Enviroment-friendliness and low space needed is also an attractive feature.

Advantage (over current membrane systems)

-robust in organic solvents (here proposed: methylene chloride, acetone, toluene)

-also designed for high viscosity

Advantage over currently used technology (evaporation):

-low temperature, low(er) energy costs

-better product quality

-adaptable to current technology (evaporation, "flashing")-hybrid

-less or other fouling that may be better controllable (also evaporation has fouling)

We will discuss work on the removal of solvents and possible use in processing of oils and fats industry. A special pilot is on acetone recovery from seed oil fractionation plan has been built. On this system extensive piloting is done and still in progress.

Mixed Matrix Membrane for Protein Separation.

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In this study, strontium-substituted nano hydroxyapatite (Sr-HAP) was synthesized by ultrasonic method. The surfaces of Sr-HAP particles were grafted with acrylic acid (AAc) by low temperature plasma technology and Sr-HAP grafted with AAc (Sr-HAP-AAc) was obtained. The dual layer polyether sulfone (PES)/HAP mixed matrix membranes (MMMs) were prepared by an immersion phase separation process. A particle free PES membrane layer was co-cast with the active support layer, which led to formation of dual layer MMMs. The active support layer consisted of Sr-HAP-AAc particles embedded in macroporous PES. The dual layer MMMs showed separation of protein via diffusion as well as adsorption. The bovine serum albumin (BSA) was used as a model protein. The BSA adsorption capacity of MMMs increased with extending equilibrium time and almost reached stable at 20 h. The BSA adsorption capacity of dual layer MMMs was 48.6 mg/(g MMMs). The dual layer MMMs with top PES layer kept good filtration and adsorption properties.

201 Adsorption Behavior and Self-Aggregation of 5,10,15,20-Tetrakis-(4-sulfonatophenyl)-Porphyrin on Quaternized Polysulfone Membrane.

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202 Free Diffusivity of Viruses: Experimental Measurements and Model Predictions.

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204 Functionalization of Silica Membranes with Lipid Bilayers for Sugar Recovery.

Shanshan Zhou, *Daniel Schlipf, Stephen E. Rankin, and Barbara L. Knutson*
Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY

205 Living Biofilm-Resistant Membranes.

Manish Kumar[1], *Thammajun L. Wood*[1], *Rajarshi Guha*[1], *Li Tang*[2], *Michael Geitner*[2], *and Thomas Wood*[3]
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206 A Weak Cation Exchange Macroporous Hydrogel Membrane for Monoclonal Antibody Capture.

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A Novel Method for the Covalent and Site Specific Immobilization of Proteins.

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Protein immobilization is an important step of bioengineering. The attachment of functional proteins onto a solid support or inside a polymer matrix is usually necessary to exploit the activity of the protein. However, proteins can easily denature and lose their function during these manipulation. Maintaining the protein structure, stability, and activity are the major challenges during the development of immobilization technology. Here we developed a method to covalently and site-specifically attach bioactive proteins through the metabolic incorporation of a non-natural amino acid azidohomoalaine (AHA). Due to its structural similarly to methonine, AHA can be used to replace methionine in protein synthesis. In the next step, AHA-containing protein can be covalently immobilized through its bio-orthogonal reaction to an alkyne group via the well-established click chemistry. Using a pyrophosphatase PpaC as the model protein, we demonstrated that the protein activity was not affected by the AHA incorporation. However, since the location of methonine residues are usually inside the folded protein structure, the limited accessibility prevented efficient immobilization. Therefore, we designed and introduced a novel methionine tag at the C-terminus of the protein and shown that the tag could be used to attach PpaC to a supporting matrix via AHA incorporation and subsequent click chemistry reaction. We expect this method and the methionine tag to be generally useful to a broad range of proteins including membrane proteins. Our future plan include the application of this method into the construction of functional biomimetic membranes.

207 Concentrating Membrane Proteins without Concentrating Detergent Using Ultrafiltration.

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Antibody Purification from Cell Culture Supernatant Using New Polymeric Multimodal Membranes.

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This poster will describe our latest research efforts on devising improved methods to capture and purify antibodies from cell culture supernatant using overload and elute chromatography with new multimodal membranes (MMMs). The membranes incorporate functional groups that provide orthogonal modes of interactions, which dramatically increases the range of ionic strength for operation of these membranes relative to conventional ion-exchange and hydrophobic interaction chromatography media, and makes them attractive candidates to face emerging challenges in downstream processing of biologics...

Protein binding experiments with IgG show the MMM has a high equilibrium binding capacity (180 mg IgG/ml) and excellent salt tolerance. It maintains binding capacities in excess of 100 mg IgG/ml at salt concentrations that are typical for elution buffers used in multi-stage chromatographic bioseparation processes. Protein dynamic binding capacities in excess of 50 mg IgG/ml were determined from breakthrough curve analysis.

In one study, the MMMs were used as the stationary phase following a Protein A purification step in the purification human IgG1 from Chinese hamster ovary (CHO) cell culture supernatant. The MMM stationary phase greatly enhanced load productivity compared to resin-based ion-exchange media. Further, no buffer exchange step was required between the Protein A and MMM chromatography purification steps.

In a second study, the MMMs were used as the stationary phase for the primary capture step, in place of Protein A resin chromatography. By loading the same column volumes of feed solution, the MMMs demonstrated a high selectivity for capturing human IgG from CHO cell culture supernatant. A high quality protein product was obtained from the MMM chromatography purification step.

This work shows that the new MMM chromatography operation can effectively decrease the number of purification steps and shorten the purification time and/or increase load productivity in downstream processing of biologics. It further shows that the new MMMs may be suitable for capture step purification of non-mAb proteins or when Protein A cannot be used.

The Effects of Filtration Condition on Virus Clearance.

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Validation of adequate virus clearance is critical in order to obtain FDA approval for a manufacturing process. Clearance can be due to inactivation or removal from the process stream. During the purification, manufacturers of monoclonal antibodies must demonstrate reduction of 10^3 to 10^5 or more virus particles than is estimated in a single dose equivalent of the unprocessed bulk. Depending on the antibody titer, estimates of the number of virus particles in a single dose equivalent could be as high as 10^{10} to 10^{15} retrovirus-like particles per mL. In addition to the removal of adventitious virus, using model parvovirus is required. Today unit operations such as virus filtration are frequently used to validate virus clearance.

Virus filtration is conducted industrially in dead end mode. Membrane performance is shown to be affected by feed pH, ionic strength and feed buffer components. Since virus filtration experiments using model mammalian viruses are expenses, complicated to run and time consuming. The purpose of this work was to determine if model bacteriophages Phix174 and PR772 can be used to rapidly determine the effect of operating conditions on membrane performance. The clearance of two model bacteriophages was tested using 30, 100 and 300 kDa polyethersulfone (PES) membranes. Flux and virus clearance were measured through the dead-end filtration experiments. The presence and concentration of Bovine Serum Albumin (BSA) and Lysozyme on the virus removal were investigated. In addition, the effects of pH on virus removal and filtration flux were determined. Our results show that 100 kDa PES membrane performs the best with regard to filtration flux and virus clearance performance in the presence and absences of tested proteins. Feed concentration close to neutral leads to a higher flux while virus titer stays more or less the same compared to other pH conditions. Mechanisms and insights on the effects of proteins and pH on virus removal are obtained.

209 Protein Adsorption and Desorption of pH-Responsive Membrane Based on Ethylene Vinyl Alcohol Copolymer.

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Development of Polybenzimidazole Nanofiltration Membranes with Biomimetic Surfaces.

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Aquaporins are membrane protein water channels present in cells, and they restrict the passage of contaminants including bacteria, viruses, minerals, proteins, DNA, dissolved gases, salts, detergents, and even protons without preventing the passage of water. Small molecules such as urea and boric acid, the removal of which is inefficient by conventional membranes are also rejected. Biomimetic membranes, an innovation in water filtration technology attempts to replicate a natural process occurring at the cell level; specifically, the highly-selective and efficient transport of different molecules across a cell membrane. Therefore, aquaporins have received worldwide attention because of their potential to form biomimetic membranes with high flux and selectivity for water reuse and desalination. However, challenges involved in the incorporation of aquaporin proteins in membranes limit their applicability. One of them is to attach aquaporins to the membranes without chemically altering or damaging the aquaporins during the binding to the membrane. The second challenge is to design and prepare an assembly that allows biomimetic membranes with aquaporins to sustain hydraulic water pressure gradients without losing their integrity and performance. The overarching objective of this project is to form a biomimetic membrane made of unaltered aquaporins dispersed in a polymeric membrane selective layer and capable of operation under high hydraulic pressure. To this end, polybenzimidazole (PBI) membranes were surface modified with treated aquaporins in order to achieve higher water flux and selectivity. Membranes modified with aquaporins displayed lower flux declines and higher flux recovery values after backwash as compared to unmodified PBI membranes. Also, modified membranes showed improved rejection values for both protein and salt solutions of different concentrations. However, there was leakage of ions between the channels. Therefore, in order to improve the rejection of protons, ions and other impurities, aquaporin channels were aligned with the direction of water flow. Functional groups were installed on AqpZ for covalent attachment to the polymer matrix so that the proteins could be immobilized to the membranes and aligned in the direction of the flow.

210 **Measurement of Aquaporin Z Compatibility with Biomimetic Membranes Using a Developed Membrane Protein Compatibility Evaluation Method.**

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212 **Functionalization of Silver Nanoparticles on Membranes and Its Influence on Biofouling.**

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Functionalization of Membranes with Ompf Porins.

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Even more impressive than artificial membranes are the biological membranes that nature offers, with higher selectivity, resistance to fouling, and regenerative capabilities. Thus, incorporating into membranes the structures responsible for high biological performance could potentially increase stimulus-responsive behavior and salt rejection while attaining larger fluxes than other highly selective membranes. In order to achieve proper alignment and stabilization of biomolecules, certain techniques are utilized. This research first explains the process and behavior of layer-by-layer assembly of polycations and polyanions. Multilayers of electrolytes have been shown to increase the number of immobilized biomolecules by 25-fold with insignificant distortion of biomolecules.

Porins, or cylindrical beta barrel protein pores, are the biomolecule of interest in this research. Membranes with solely porins acting as their channels could produce novel behaviors and transport only small metabolites while rejecting macromolecules. These beta barrel proteins are immobilized within the pores of polyvinylidene fluoride (PVDF) membranes using layers of poly(acrylic acid) (PAA) hydrogel intercalated through in situ free radical polymerization and poly(allylamine) hydrochloride (PAH) accumulated during convective flow. The major challenge with this study is achieving an orientation of the porins parallel to the length of membrane pores so fluids may flow through their channels. This poster examines methods of functionalizing the membranes with OmpF porins from *Escherichia coli* and characterization of the membrane during each stage of the process, including zeta potential analyses, pH responsiveness, changes in flux, and sugar rejection. Characterization of solutions containing OmpF porins is also expounded.

Acknowledgement: This research is made possible by NSF KY EPSCOR and by NIH-NIEHS-SRC.

213 Nicotine Delivery Via Programmable Carbon Nanotube Membrane Transdermal Delivery Devices.

Lily Berger
Materials Science & Engineering, University of Washington, Seattle, WA

214 Dynamic Electrochemical Membranes for Cyclic Protein Transport.

***Daniel Shea**, Susrut Akkineni, and Bruce J. Hinds*
Materials Science and Engineering, University of Washington, Seattle, WA

215 Ultrafiltration to Concentrate Membrane Proteins without Concentrating Detergents.

***Hasin Feroz**[1], Craig Vandervelden[2], Bon Ikwuagwu[3], Bryan Ferlez[4], Carol S. Baker[5], Mariusz Grzelakowski[6], John H. Golbeck[7], Andrew L. Zydney[8], and Manish Kumar[8]*
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POSTER SESSION V - MEMBRANE MATERIALS, MODELING, AND OTHER NOVEL APPLICATIONS

217 Fabrication and Characterization of Polybenzimidazole-Multiwall Carbon Nanotubes Composite Membrane for Gas Separation.

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Nanoporous Metallic Films As Components of Composite Membranes.

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Magnetron sputtering is a physical vapor deposition method that allows the deposition of thin films of different materials on a variety of substrate materials. Sputtering allows fine control of the film thickness and composition through co-sputtering from multiple target materials. As part of this study thin films have been sputtered on top of microfiltration polysulfone membrane substrates. The resulting composite membranes have remained permeable under testing with deionized water. The base Nanostone PS35 membrane showed permeability of 1941 LMH at 1.7 bar, while the membrane-film composite had a permeability of 163 LMH at 1.7 bar.

Thin films of metallic alloys deposited in this way can be made nanoporous through a process called dealloying. The process involves the removal of the less noble component of an alloy by an etchant creating an open nanoporous structure. The pores created by this method commonly vary from a few nanometers to a few hundred nanometers.

This research focuses on using magnetron sputtering to deposit precursor metallic alloy films from 100 to 250nm thick on top of porous membrane substrates. These dense precursor films are then dealloyed to produce pore/ligament structures of approximately 10nm characteristic size. In these studies iron and palladium were chosen as a precursor alloy. A portion of the iron is etched away with sulfuric acid to generate a nanoporous structure. Fe/Pd nanoparticles have been used with success to dechlorinate various chlorinated organic compounds (COCs) for wastewater treatment purposes. Nanoporous Fe/Pd shows promise to be similarly reactive with COCs due to its high surface area and curved structure. Taken together this means the composite membrane produced by fabricating a high surface area, porous Fe/Pd film on top of a microfiltration or nanofiltration membrane substrate shows promise both as a catalyst and as a platform for separations.

This project is funded by NIH-NIEHS-SRC and by NSF KY EPSCOR at the University of Kentucky.

Novel Amphiphilic Zwitterionic Copolymer Membranes of ~ 1nm Pore Size for Industrial Wastewater Treatment and Reuse.

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Membranes with ~1 nanometer effective pore size that allow removal of high oil/organic content (dyes, industrial chemicals, surfactants etc.) have numerous applications in the treatment of wastewater from textile plants, oil refineries, fracking and oil extraction. The small effective pore size of such membranes can potentially provide better effluent quality and prevent the environmental release of a wider range of pollutants. However, there are very few commercial membranes in this pore size range, and those that are available exhibit poor selectivity, charged surfaces which lead to complex separation mechanisms, and fouling due to the accumulation of feed components on the membrane surface. In addition to high flux, sharp selectivity and exceptional fouling resistance to common foulants in wastewaters, membranes for these applications should also have high chemical resistance and be easily fabricated into large-area membranes. Zwitterionic groups have been shown to strongly resist biomacromolecular fouling due to their high degree of hydration, which makes them promising for membrane applications. We have introduced a new class of membranes whose selective layers are made of self-assembling zwitterionic amphiphilic random copolymers. These membranes derive not only fouling resistance but also their permeability and selectivity from this self-assembled nanostructure. In this study, we evaluate the potential and performance of these new membrane materials in wastewater treatment. We synthesized random copolymers of a hydrophobic monomer (trifluoroethyl methacrylate) and two zwitterionic monomers (sulfobetaine methacrylate, phosphobetaine methacrylate) by free radical polymerization. These copolymers self-assemble into bicontinuous networks of ~1 nm nanochannels, driven by the strong electrostatic interactions between the zwitterionic groups, and documented by transmission electron microscopy (TEM). Membranes manufactured by coating these copolymers on commercially available support membranes exhibit size-based selectivity with a ~1 nm size cut-off demonstrated by filtering negatively charged dyes. We have studied how feed composition such as ionic strength and presence of foulants in varying wastewater streams affects membrane performance. Specifically, we have tested the performance of these membranes by filtering single foulants, and simulated wastewater feeds. These membranes are extremely resistant to fouling by proteins and oil emulsions, fully retaining their permeability even during the filtration of the foulant solution in dead-end mode for up to 7 days. They are also stable in a wide range of chemical solutions: salt solutions (upto 1M NaCl), acidic and basic buffers, as well as chlorine. They exhibit a sharp, size-based cut-off for organic molecules such as dyes found in textile wastewater. Their low salt rejection allows operation at lower pressures. These results indicate the promise of this new family of membrane materials for industrial wastewater treatment, reclamation and reuse.

Preperation and Characterization of Cation/Anion Exchange Membrane for Electroadsorption-Deionization Process.

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The electrodeionization process is a mixture of ion exchange resin method and electrodialysis. There are a cation exchange membrane and an anion exchange membranes for electrodialysis, and cation and anion exchange resin filling in between two films to prepare a module. And Homogenous size distribution and the equivalent ratio of the ion exchange resin are also very important factor in determining the performance of the module. On the basis of these point, EAD (Electroadsorption-deionization) process module using the bipolar membrane with the ion exchange resin is produced thesedays. We prepared on the rubber polymer to improve the ion exchange capacity than the module currently produced. So, Sulfonated and aminated SEBS polymer (Poly styrene-ethylene-butylene-styrene triblock copolymer) was used to prepare the cation and anion exchange membrane in the module. Thus, this study is information on the cation and anion exchange membrane prepared blending the particles introduced into the ion exchange capacity and the high ion exchange capacity polymer to improve the performance of the module.

218 Fabrication of a Superhydrophilic PVDF Based Membrane Using a Facile Prefabricated TiO2 Nano-Particle Surface".

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A Sequential Use of UV/H2O2 – (PSF/TiO2/MWCNT) Mixed Matrix Membranes for Removal of Dye from Aqueous Solution.

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Performance of a hybrid UV/H_2O_2 – Mixed matrix membrane system for an azo dye, Acid Black 1 [AB1], removal in a water purification process was studied. Different mixed matrix membranes embedded with titanium dioxide (TiO_2) nanoparticles, multi-wall carbon nanotubes (MWCNT), and a mixture of them were fabricated by the phase inversion method. Mixed matrix membranes embedded with MWCNTs resulted in higher pure water flux, and mixed matrix membranes embedded with TiO_2 showed lower flux declines in the presence of AB1. However, all the membranes exhibited very low Total Organic Carbon (TOC) rejection and none of the mixed matrix membranes could decolorize the AB1 solution. UV/H_2O_2 pretreatment of the AB1 solution resulted in enhanced TOC rejection, decolorization and enhanced anti-fouling membrane behavior. Combining UV/H_2O_2 with each type of polysulfone (PSF) mixed matrix membranes (PSF/TiO_2, PSF/MWCNT and PSF/TiO_2/MWCNT) resulted in optimal performance in terms of permeation, flux decline, antifouling, rejection and decolorization. The hybrid process of UV/H_2O_2-PSF/TiO_2/MWCNT mixed matrix membrane resulted in 270 ($L.m^{-2}.h^{-1}$) permeation, 29% flux decline, 90% TOC rejection, 99% decolorization and 99% Flux Recovery Ratio (FRR %).

219 The Potential to Enhance Membrane Module Design with 3D Printing Technology.

Jian-Yuan Lee
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220 Theoretical Study of Fluid Flow through Screened Channel in a Tangential Flow Filtration Process.

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221 Weak Polyelectrolyte Multilayers As Tunable Membranes for Solvent Resistant Nanofiltration (SRNF).

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Boldly Going Where No UV Has Gone before: Producing UVC inside Membrane Modules Via X-Ray Radioluminescence for Biofouling Prevention.

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We are exploring methods for producing germicidal UV radiation inside spiral-wound RO modules to directly inactivate bacteria and potentially provide a more robust method for reducing, or even eliminating biofouling in water treatment applications. The technology employs UVC-radioluminescent (RL) materials incorporated onto the feed spacers which can be activated by irradiation through the module with hard X-rays via an external X-ray source. We have demonstrated 2-log bacterial inactivation using UVC-RL materials at modest X-ray doses, and additionally studied the impact of X-ray and UVC irradiation on membrane integrity. Our ongoing work involves studying the impact of X-ray photon energy on module penetration and phosphor excitation. Progress towards prototype development and achieving an effective and affordable antifouling technology will be analyzed and discussed.

The Effect of Sulfonated Polysulfone on the Compatibility and Structure of Polyethersulfone-Based Blend Membranes.

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Polymer blend is the most common method to improve membrane hydrophilicity, in which the compatibility between the polymers is an important factor affecting the structures and properties of blend membranes. Polyethersulfone (PES)-based blend membranes were prepared from PES/polysulfone (PSf)/N, N-dimethylacetamide (DMAc) and PES/sulfonated polysulfone (SPSf)/DMAc casting solutions with water as coagulant via immersion precipitation phase inversion, respectively. The compatibility of blend systems and membrane formation process were investigated through thermodynamics and kinetics analyses. Ultrasonic through-transmission measurements were performed to quantify the rate of membrane formation during the phase inversion process. The effect of SPSf on the compatibility and morphologies of PES-based blend membranes were characterized by scanning electron microscopy (SEM), pure water flux and BSA

rejection. Results indicated that the PES/PSf blend system was partially compatible, leading to instantaneous demixing and the obtained membrane with finger-like structure, whereas the PES/SPSf blend system was entirely miscible, resulting in delayed demixing and the obtained membrane with sponge-like asymmetrical gradient structure. Simultaneously, the surface segregation behavior of SPSf with hydrophilic sulfonic acid groups during mutual diffusion process resulted to the enhancement of PES/SPSf membrane hydrophilicity. Consequently, PES/SPSf blend membrane showed excellent water permeability and better antifouling ability.

222 Study on Insoluble Polyimide Solvent-Resistant Nanofiltration Membranes Fabricated By a Two-Step Method.

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223 Permeation-Deformation Relationships for Porous Polymer Membranes.

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224 Phase Inversion Kinetics of Polymer- Ionic Liquid Solutions in Relationship with Membrane Morphology and Macrovoid Formation.

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228 Cellulose Membranes for Organic Solvent Nanofiltration.

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Concentration and Recovery of Ionic Liquids from Aqueous Solutions By Nanofiltration.

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Ionic liquids (ILs) have been considered as a class of promising solvents for dissolution of natural polymer such as cellulose, silk, and wool chitin as well as raw biomass like lignocellulose and crustacean shells due to their high dissolving capacity of biopolymer. Given the fact that ILs are much more expensive than conventional solvents, it is of significance to recycle ILs during the dissolution of natural polymer and raw biomass.

In this work, the filtration behavior of three ILs ([AMIM]Cl, [BMIM]Cl and [BMIM]BF_4) in aqueous solutions by two nanofiltration (NF) membranes (NF90 and NF270) were investigated. The experimental results showed that the permeate flux increased linearly with the pressured applied at a constant IL concentration and decreased with the IL concentration at a constant pressure. Compared to NF270 membrane, NF90 showed the higher rejection because of its smaller pore size. For both membranes examined, the retention of IL was in the order of [BMIM]Cl > [BMIM]BF_4 > [AMIM]Cl, and was inversely proportion to the IL diffusion coefficients in water. The experimental results indicated that the organic cation in IL had an important effect on the IL rejection because of its larger size compared to anion. The permeate fluxes of ILs were calculated using the solution-diffusion transport model coupled with film theory. The results showed that this approach was able to calculate the permeate fluxes of ILs for IL/H_2O mixtures studied. Under the optimal experimental conditions determined in the present work, [BMIM]Cl in the aqueous solution could be concentrated to 18.85 wt% from its initial concentration of 5 wt% using the NF90 membrane, and a recovery of around 96% was obtained. The outcome of the present work will provide necessary guide for the application of concentrating ILs in aqueous solutions by nanofiltration.

Direct Observation of Gel Deposit Dynamics on Nanofiltration Membranes.

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Membrane-based water production can be severely limited by organic and biological fouling, the prevention and management of which is a long standing theme of research.

Such fouling materials are often characterized by gel structures comprised of long chain polymers such as polysaccharides. Here, we report a direct observation method that was used to monitor alginate fouling and cleaning with the aid of fluorescent marker beads. These markers are trapped in the alginate layer and their motion is hindered due the visco-elastic medium. Observation of these marking particles trapped at various distances from the membrane, enables to follow the micro-rheology and formation kinetics of the deposited layer.

Fouling and cleaning experiments were conducted with and without the presence of calcium, enabling controlled manipulation, albeit qualitatively, of gel rigidity – the presence of calcium ions forms a more rigid alginate layer, which is manifested through the near immobilization of the marker beads; this is contrasted by the more fluid-like layer formed in the absence of calcium. Interestingly, rigidity of the deposited 'gel' correlated with a faster permeate flux decline. Finally, direct observation experiments suggest that detachment occurs more rapidly and completely when the applied pressure is shut off, while significantly less detachment was observed when only the permeation flux was shut off during a cleaning stage. This insight into the dynamics of 'soft', deformable deposits reveals interesting mechanisms of fouling and important implications for the development of efficient cleaning protocols.

Influence of Imogolite Nanotubes on the Structure and Performance of PVA and Psf Nanocomposite Membranes.

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Presentation Title: Influence of imogolite nanotubes on the structure and performance of PVA and PSf nanocomposite membranes.

Authors: Ming Li and Jonathan Brant

Abstract: Engineered nanomaterials, imogolite nanotubes, have been used to improve the mechanical strength and performance (flux and selectivity) of membranes used in desalination processes. Enhanced flux is purported to result from water transport through nanotubes because of their unique geometry and chemical properties. Though promising results have been obtained with carbon nanotubes, these materials are not without their drawbacks, namely cost, clumping and poor loading in polymer films. The structures and chemical properties of imogolite nanotubes are highly desirable for to further the application of nanocomposite membranes. Our presentation will cover the relationships between imogolite nanotube properties, namely length, throat diameter, and surface (inner and outer) functionalities, on water flux and ion rejection. Membrane performance is evaluated using pressure-driven filtration and thermaly-driven configurations with an emphasis on treating high-salinity waters (TDS > 50,000 ppm), representative of oil and gas produced waters. Membranes are synthesized using the following base polymers: poly (vinyl alcohol) (PVA) and polysulfone (PSf). Nanotube dispersion will be evaluated in these two polymers and the resulting impacts of these variables on membrane

performance. The change of membrane robustness and surface chemistry by adding imogolite nanotubes will also be discussed.

231 **Carbon Nanotubes/Polyethersulfone (CNT/PES) Nanocomposite Membranes Fabrication and Characterization.**

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232 **Charged Nanopore Membranes By Amphiphilic Random Copolymer Micelle Assembly.**

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233 **The Effect of Pore Penetration on Composite Membranes.**

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234 **The Effect of Pore Entrance on the Particles Concentration Profile in Porous Membranes.**

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Abstracts:

237 Nanoparticle Deposition with Controlled Density and Placement.

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Transport of Deformable Particles in Porous Media.

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Filtration is critical to the purification in food and residual water in fossil fuels industries. In the pharmaceutical industry, new drug delivery techniques to transport and deliver drugs in a more efficient way use a filtration process in the fabrication and purification of liposomes—small, soft vesicles formed by a lipid bilayer that encapsulate a water solution where the drugs are stored. And in a similar vein, new designs of microfiltration devices are used to capture circulating tumor cells, and then be able to design better treatments. In all these cases, the transport of soft colloids, soft vesicles and other small deformable particles through the tortuous network is a key figure-of-merit. To further the ability to design membranes for fractionation of deformable particles, we have developed a (2-d) computational multiscale approach. We use a combination of the extended finite element method to describe the creeping fluid flow ($Re \sim 0$) inside a portion of a filtration membrane with an embedded interface, coupled with a particle method that interpolates the particle's membrane (interfacial) position and corresponding fields using least square fitting.

We have now modeled (in 2-d) how the combination of porous network geometry (porosity, pore size, and connectivity) and soft particle deformation-related properties (elasticity and surface tension) influence the particles' sieving coefficients. The focus in this paper is on the relationship between the elasticity of the particle and the porosity of the system, and its effects on the overall permeability of the system (and the sieving of the particles). First we present the base case of two immiscible fluids (such as an oil droplet in water), and show that the transport of such particles consistently scale with the concepts of a critical pressure gradient across the pore being determined by the ratio of the particle and pore diameter and the interfacial tension, as has bee analytically derived for the case of an axisymmetric spherical droplet entering a capillary. The base case of a single pore and droplet is then extended to include arrays of obstacles (creating a porous network) and multiple droplets. In this case, the applied trans-network prerssure drop is not the same presssure gradient each droplet experiences when it needs to deform to pass between obstacles. These cases provide a separate set of scaling rules that can guide membrane design for fractionation purposes.

Finally, and most importantly we examine the difference between the simple immiscible droplet and an elastic particle. In the former case, the "penalty" for deformation is in creating curvature, while in the latter case the deformation requires creation of surface area. Thus, we find that

- elastically deformable particles have different modes of deformations, and

- the pressure landscapes on their permeation are drastically different than surface tension based particles.

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Alkali Metal Chloride Sorption in Cross-Linked Polymer Membranes.

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Preparation of Attapulgite-Silver-Nanoparticles and Its Application on Fabricating Antimicrobial Thin-Film Composite Membranes.

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In this study, a novel way of preparation of attapulgite (AT)-Silver-nanoparticles (AT-AgNP) composite powder via a non-chemical-reduction method was achieved by blending attapulgite suspension and silver nitrate solution, followed by heat-stirring treatment, spray drying and calcination process. The prepared AT-AgNP was used for fabricating antimicrobial NF and RO membranes.

It was firstly studied the effect of preparation process on the formation of AT-AgNP. XRD was used to analyze the structure and chemical composition of the composite powder, SEM and TEM were used to characterize the nano-silver in the composite powder, and TGA and FTIR were used to analyze the formation mechanism of nano-silver.

The results showed that attapulgite-nano-silver can only be obtained by first stirring the AT suspension and $AgNO_3$ solution at elevated temperature, then spray drying the mixture and finally calcining the sprayed powder at a temperature above 200℃. The formation mechanism of nano-silver is correlated with the formation of Ag_2CO_3, which was formed by the reaction of CO_3^{2-} in the AT with the Ag^+ in $AgNO_3$ and then decomposed and covered on the surface of AT during calcination. The release of silver ions of AT-AgNP and its antimicrobial properties were measured with GC-ICP-MS and disk test method. The result showed the content of silver ions increased with increasing soaking time. AT-AgNP showd a bactericidal rate of 99.7% at the concentration of 0.5ppm.

To utilize AT-AgNP's antimicrobial properties, AT-AgNP was incorporated in the functional layer of NF membrane through interfacial polymerization. The prepared NF membrane showed a bactericidal rate of 90% at a loading of AT-AgNP 0.005% (wt/v) in the organic phase. With increasing the loading of AT-AgNP in the organic phase, the salt rejection of the prepared NF membranes decreased, and the water flux increased, indicating the incorporation of AT-AgNP may lead to defects in the polyamide separation layer.

To avoid the formation of defects in the separation layer, AT-AgNP was also added in PVA solution first, and then coated onto the surface of composite RO membranes to fabricate the antimicrobial membrane. The coated homemade RO membrane showed a bactericidal rate of 99.5%, at loading of 0.075% (wt/v) AT-AgNP in PVA coating solution and the membrane exhibited a water flux of 30.3L/m^2·h, a salt rejection of 99.4%.

Ultrafiltration Membranes Produced from Polymerization of Water/Oil/Block Copolymer Self-Assembly.

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As human population continues to grow, demands for clean water will increase, necessitating further development of water purification technologies. Ultrafiltration is a necessary step in the treatment of both drinking water and wastewater in which suspending particles, viruses, and bacteria are removed. Conventional ultrafiltration (UF) membranes are produced through non-solvent induced phase separation (NIPS). However, the NIPS technique is not ecofriendly and resultant membranes are anisotropic with low surface area and porosity. The self-assembly of block copolymers at an oil/water interface has been widely studied for applications ranging from drug delivery to energy storage. The purpose of this research is to utilize self-assembly as a template for producing mesoporous polymeric materials to be used as UF membranes. A tri-block copolymer of poly(ethylene oxide), PEO, and poly(propylene oxide), PPO, with $(PEO)_{13}$-$(PPO)_{30}$-$(PEO)_{13}$ composition is used, and different water/oil/block copolymer concentrations and compositions are studied. The oil phase consists of butyl acrylate as well as ethylene glycol dimethacrylate, a cross-linker, and can be polymerized via photo- and thermal initiators. Upon self-assembly of the water/oil/block copolymer mixture into a desired mesostructure, the oil phase is polymerized and a mesoporous polymer is obtained. Resultant materials are characterized through polarized light microscopy (PLM), rheology, BET, and small angle X-ray scattering (SAXS). The produced membranes are found to have mesopores in the range of 70 nm with improved permeability over conventional UF membranes, as measured in a dead-end flow using an oil-in-water emulsion as feed stream.

Hydrophilization of Hydrophobic Membrane Surfaces By the Adsorption of Water-Soluble Polymers.

Do Hyiung Shin, Yi Seul Jeon, and ***Ji Won Rhim***
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The adsorption of biological compounds such as proteins on membrane surfaces which is driven by different protein-surface forces, including van der Waals, hydrophobic and electrostatic forces, is important in the fields of separation science. The physical adsorption of natural polymers such as proteins on hydrophobic surfaces is referred to as a part of 'fouling phenomena', which is a major drawback of the continuous flux decline due to the adsorption in question, pore blocking, precipitation and cake formation in membrane-based water purification processes. The low surface tension energies of hydrophobic membrane surfaces give rise to several problems of easy wetting, ease of initial flux, adsorption or spreading. Therefore, it is required that the surface energy should be increased through the introduction of polar functionality using chemical modification, gas-discharge treatment (plasma, corona, etc., g-radiation, UV irradiation, and coating. Since, however, these chemical approaches are limited to lab scale to date because of the complicated production equipments, strict operation requirements and high costs, the coating or impregnating with hydrophilization agents, such as alcohols, surfactants, or amphiphilic polymers is more favorable method to endow the hydrophilicity with hydrophobic membranes.

In this study, to improve the water flux of porous hydrophobic membranes, various water-soluble polymers including neutral, cationic and anionic polymers were adsorbed using 'salting-out' method. The adsorbed hydrophobic membrane surfaces were characterized mainly via the measurements of contact angles and scanning electron microscopy (SEM) images. To enhance the durability of the modified membranes, the water-soluble polymers such poly(vinyl alcohol) (PVA) were crosslinked with glutaraldehyde (GA) and found to be resistant for more than 2 months in vigorously stirred water. The water flux was much more increased when the ionic polymers used as the coating materials rather than the neutral polymer and in this case, about 70% of 0.31 $L/m^2 \cdot h$ (LMH) to 0.50 LMH was increased when 300 mg/L of polyacrylamide (PAAm) was used as the coating agents. Among the cationic coating polymers such as poly(styrene sulfonic acid-co-maleic acid) (PSSA_MA), poly(acrylic acid-co-maleic acid) (PAM) and poly(acrylic acid) (PAA), PSSA_MA was found to be the best in terms of contact angle and water flux. In the case of PSSA_MA, the water flux was enhanced about 80%. The low concentration of the coating solution was better to hydrophilize while the high concentration inclined to block the pores on the membrane surfaces. The best coating condition was found: (1) coating concentration 150 to 300 mg/L, (2) ionic strength 0.15, (3) coating time 20 min.

Fabricaiton of Hierarchically Structured Helical Micro/Nanofibrous Nonwovens and Its Mechanism Study.

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Electrospinning and melt blowing are the most commonly used technologies to produce micro/nanofibrous nonwovens. Helical fibers resembling plant tendrils in micro/nanoscale have been of increasing interest because of their unique characteristics. The introduction of helical structures into the micro/nanofibrous nonwovens finds potential applications in fields such as micro/nanoscale sensors, filtration materials, and oil sorbents. The three-dimensional structure of the helical fibers can provide the nonwovens larger specific surface area, larger porosity, and better mechanical properties in terms of resiliency and flexibility. In this study, we report the fabrication of micro/nanoscale helical fibers by electrospinning and melt blowing. Two kinds of polymer, an elastomeric component and a rigid component, are combined in the electrospinning and melt-blowing processes to produce helical fibers. A Core-shell spinneret is used in electrospinning. While during melt blowing, a swirl-die is adopted. Due to the different shrinkages displayed by the two components, helical fibers with three-dimensional spiral shape are formed after electrospinning and melt blowing. This work can provide a promising technique for producing micro/nanofibrous materials with helical fiber morphology.

239 Antifouling Modification of Ultrafiltration Membranes By Grafting Polyzwitterionic Brushes.

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240 Mechanical Enhancement of Thin-Film Composite Membranes Using Helically-Coiled Carbon Nanotubes for Engineered Osmosis.

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Special Applications of Nanofiltration Membranes.

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Nanofiltration membranes have established itself as a mainstay in many applications involving drinking water and beverage manufacturing. However, their use in other special applications is not often discussed in literature. This study takes on the challenge of applying commercial nanofiltration membranes for various separation/concentration processes with growing commercial interest. NE70 (Toray Chemical CSM) nanofiltration membrane reduced COD and BOD found in landfill leachate treatment water from 5,400ppm to 180ppm and 3,400ppm to 50ppm respectively. Polysaccharides with low conductivity were concentrated to over 80% by using NE40 and 70 membranes. Raw materials used in the cosmetics industry were concentrated using NE70 membranes with significant energy savings as compared to traditional thermal fractionation techniques. In order to recover valuable ions found in the chlor-alkali wastewater, NE70 membranes were used to selectively separate out sulfate (SO42-) ions. NE70 membranes were also used to effectively separate lithium ions from other multivalent species for battery manufacturing processes. And last, nanofiltration membranes were applied to concentrate glyphosates, most often used in pesticides, from 0.1% up to 2.5% via a membrane de-watering process.

241 Modification of UF Membranes with a Polyampholyte Hydrogel for Fouling Mitigation.

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The Department of Desalination & Water Treatment, Ben-Gurion University, Sde Boker, Israel

N/A Zwitterionic Modification of Ultrafiltration PVDF Membranes for Improved Fouling Resistance.

242 One-Step Synthesis of Hybrid Zeolite Membranes Containing Catalytic Metal Nanoclusters.

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Preparation of PVDF UF Membrane Using Lithium Chloride and Amphiphilic Block Copolymer Via Non-Solvent Induced Phase Separation.

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Preperation and Characterization of Novel Polyetheretherketone Based Polymer Cation Exchange Materials.

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Department of Materials Engineering and Convergence Technology, Gyeongsang National University, JinJu-si, Korea, Republic of (South)

Preperation and Morphological Control of Porous Polybenzimidazole Membrane.

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Pulsed Low Energy Positron System (PLEPS): A Promising Tool to Investigate Dispersion in Mixed Matrix Membrane.

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Itami[2], *and Ivo F. J. Vankelecom*[1]
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N/A **Fabrication of Hierarchically Structured Helical Micro/Nanofibrous Nonwovens.**

Conditioning Membranes for Improved PRO Performance.

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Maximizing energy production from PRO starts with designing membranes that are able to withstand PRO conditions. An appropriately designed PRO membrane exhibit high water permeance to limit resistance to water flux, excellent salt rejection to maintain the osmotic driving force, low structure parameter to minimize internal concentration polarization (ICP), and robust strength to withstand the required hydraulic pressure.

There are multiple trade-offs for making PRO membranes, however. As is typical with many membrane processes, increasing selectivity to reduce ICP will generally result in lower water permeance. Making low structural parameter membranes (thin, highly porous support layers) make them less tolerant to pressure. A low structural parameter may also make the membrane susceptible to severe compaction (which would ultimately enhance ICP). These tradeoffs make approaching membrane performance from a membrane design standpoint challenging.

We have recently identified a method of conditioning an existing membrane prior to PRO testing that resulted in improved overall PRO performance (higher water flux, lower salt flux, and higher power density). By conditioning the membrane under 150 psi pressure (essentially in RO) for 2 hours prior to testing under relevant PRO conditions, water flux increases by 17% and salt flux drops by an astonishing 85%. We believe this low pressure RO treatment may "heal" defects in the membrane through modest fouling caused by particles and organics present in any membrane system. The fouling results in a slightly lower permeance, which mitigates some of the water flux improvements in PRO, the lower salt flux lessens ICP. The results suggests that better utilization of osmotic pressure is possible in PRO systems when the membranes can be conditioned under pressure.

247 **Composite Self-Assembled Block Polymer Hollow Fiber Nanofiltration Membranes with Chemically-Tailored Pore Walls.**

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Cellulose Membranes and Their Derivatives: Modeling of Casting Methods.

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This project seeks to characterize the properties of experimental cellulose derivatives and their effect on membrane casting. Properties linked to several categories of derivatives ranging from cellulosic ester to nanocellulose have been investigated. As well as their corresponding casting methods including dry wet spinning and phase inversion by means of evapoporametry, tangential flux filtration, tensile strength, and FTIR. Additionally, data of physical and chemical alterations to the casting technique of cellulosic membranes have been examined and summarized.

248 Rapid Uranium Isotopic Analysis Using Ultrafiltration Membranes and Alpha Spectroscopy.

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Growth-Front Monolayer Plating of Precious Metals through Insulating Mesoporous Supports.

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Monolayers of precious metals are deposited within the pores of insulating mesoporous membranes via a new electrochemical underpotential deposition growth front mechanism. A gold electrode is evaporation deposited onto one membrane face and a monolayer of copper is underpotentially deposited through the membrane and to the top surface, followed by spontaneous galvanic replacement of copper by platinum or iridium. Detection of precious metal on the opposite membrane face via XPS surface analysis and quantification of areal density by ICP-IES demonstrates a novel copper monolayer *growth front* plating mechanism through the pores. Catalytic water splitting for hydrogen generation is demonstrated for applications including polymer electrolyte membrane fuel cells, hydrogen generation, flow battery energy storage, and electrocatalytic conversions.

N/A **Low Fouling Membrane.**

Surface Energy Enhancement of Poly(butylene terephthalate) By Addition of TiO2 and Polyhedral Oligomeric Silsesquioxane (POSS) Nanoparticles.

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The presence of water droplets in fuels is a major factor affecting the performance of diesel engines, contributing to fuel system corrosion, fouling and performance degradation. Coalescing filters are efficient and effectual for the removal of water drops from fuel. One disadvantage of the filtering approaches is that the hydrophobicity of fibers can cause increased liquid holdup in the filter which in turn reduces the filter's permeability. Due to its excellent chemical and mechanical properties, poly(butylene terephthalate) (PBT) largely used to produce fibers for coalescing filters, for the removal of water drops from fuel. One disadvantage of the filtering approach is the hydrophobicity of PBT fibers which causes liquid holdup in the filter, which in turn reduces the permeability. Surface energy enhancement of PBT by addition of hydrophilic fillers could decrease the hydrophobicity and modify the filters performance.

In this research, poly(butylene terephthalate) (PBT) based nanocomposites containing nano- Titanium dioxide and Polyhedral Oligomeric Silsesquioxane (POSS) nanomaterial were prepared by melt compounding. The influence of these nano materials on surface energy of the resultant nanocomposites was investigated by the use of contact angle measurement (CAM). Contact angle measurements of the resultant PBT nanocomposites showed that the wettability of such composites depends on the particular nanoparticles used. PBT/TiO2 (5 wt%) and PBT/Trisilanolethyl POSS (5 wt%) showed the lowest water contact angle and the highest wettability.

Effect of Chemical Structure on Permeability and Fouling Resistance of Self-Assembling Zwitterionic Copolymer Membranes.

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Polymer self-assembly is a promising tool for scalable manufacture of membranes while maintaining high permeability and controlled pore size. Tuning copolymer composition (chemical structure, monomer ratios) and processing methods can change copolymer behavior which can dramatically affect the self-assembly and hence the membrane performance (permeability, selectivity, fouling resistance). Membranes with ~1 nanometer effective pore size have numerous applications in the biochemical and pharmaceutical industries, as well as wastewater treatment processes. However, there are very few commercial membranes in this size range, and those that are available tend to show poor selectivity due to broad pore size distributions, and charged surfaces which lead to the rejections being affected by solute size, charge and chemical interactions between the membrane and solute. There is a need for new membrane materials that enable separation of small organic molecules while exhibiting ease of fabrication into large-area membranes. Zwitterionic groups are shown to strongly resist biomacromolecular fouling due to their high degree of hydration, which makes them promising materials for membrane applications. Studies based on zwitterionic surfactants and simulations have reported zwitterionic groups have different degrees of interaction with water. But studies on the influence of the chemical structure of zwitterionic groups on membrane performance, especially fouling resistance are rather limited. Zwitterions are also documented to self-assemble into channel-type clusters 0.6-2 nm in size. We introduce a new class of membranes whose selective layers are made of self-assembling zwitterionic amphiphilic random copolymers. These membranes derive not only fouling resistance but also their permeability and selectivity from this self-assembled nanostructure. We synthesized random copolymers of three hydrophobic monomers (acrylonitrile, methyl methacrylate, trifluoro ethyl methacrylate) and four zwitterionic monomers (sulfobetaine methacrylate, sulfopropylbetaine vinylpyridine, sulfobutylbetaine vinylpyridine and phosphobetaine methacrylate) by free radical polymerization. These copolymers self-assemble into bicontinuous networks of ~1 nm nanochannels, driven by the strong dipoles of the zwitterionic groups, and documented by transmission electron microscopy (TEM) imaging. Membranes prepared by coating these polymers on porous supports exhibit size-based selectivity with a ~1 nm size cut-off demonstrated by filtering negatively charged dyes. Performance of membranes whose selective layers are made of zwitterionic amphiphilic random copolymers depends on the zwitterionic chemical structure. By systematically varying the chemical structure of the zwitterionic monomer (anionic group, spacer length between the charges) and hence the copolymer, we have shown that for similar zwitterionic content in the copolymers, membranes formed from these copolymers have very different permeability, and fouling resistance behavior. This is attributed to the different hydrophobicities, and solubilities of the different zwitterionic groups. These structure-property relationships serve as a guideline to develop new materials for various applications such as textile wastewater treatment, pharmaceutical purification and bioseparation applications.

249 Thin Film Nano-Composite (TFN) Membrane with Metal Organic Framework (MOF) for Antimicrobial Property.

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Understanding the Roles That Patterning and Chemistry Play on Membrane Fouling.

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The fouling propensity of a membrane depends greatly on its surface properties such as chemistry and roughness. Literature and experience show that modification of membrane surfaces with appropriate chemical coatings can be effective but not sufficient for controlling membrane fouling. The discovery that sub-micron patterning of a membrane surface can improve its fouling resistance provides an orthogonal membrane design parameter.

In this poster presentation, we will describe the initial results of a collaborative experimental-modeling project aimed at developing fouling-resistant membranes. The research *hypotheses* are that (i) certain combinations of geometric patterns and chemical coatings will significantly reduce membrane fouling and (ii) experimentally-trained multiscale computational models will accelerate the discovery of new surface patterns with appropriate chemistries to improve membrane fouling resistance.

We will introduce the methodology used to pattern the membrane surfaces and report the preliminary results of a systematic study to understand how physical patterning and chemistry impact fouling propensity for colloidal foulants. Performance measurements and microscopy images will be analyzed to compare the fouling behavior of the new membranes to appropriate controls. Adsorption energies will be measured and compared to those from computational simulations.

Antimicrobial Activity of Zinc Oxide Nanoparticles in Nexar® Polymer Films.

Pietro Malky *and Lauren F. Greenlee*
Ralph E. Martin Dept. of Chemical Engineering, University of Arkansas, Fayetteville, AR

Bio-fouling on membranes, as well as in other applications including piping, container and transportation systems, continues to be a challenging problem faced by scientists and engineers. Industries face great costs trying to repair and maintain biofouled equipment, including membranes for water filtration and polymeric films used for coating applications in devices such as heat exchangers, piping systems and chemical reactors. To develop a method of controlling and potentially eliminating the possibility of bio-fouling would allow both economical and engineering relief for a wide range of industries. The process of embedding metal oxide nanoparticles in a polymer film matrix has demonstrated promising antimicrobial activity and may be used as an efficient and cost-effective method of protection against fouling and corrosion. This research focuses on developing a method of creating antimicrobial Nexar® polymer films using ZnO nanoparticles as the main antimicrobial agent. As a comparison material, TiO_2 nanoparticles will also be evaluated.

The focus of this poster presentation will be on the initial materials synthesis and development of nanoparticle-Nexar composite films. Nanoparticles will be tested at a concentration range of 1 – 20 g/L, where the nanoparticles are added into Nexar-solvent solutions before the films are cast. The Nexar polymer will be cast from two different solvents to evaluate the effect of polymer-solvent interactions on nanoparticle-polymer film formation. To test the cast films for antimicrobial activity, we will measure and report the growth of E. Coli for a 24-hr period. We will present on our results thus far regarding ZnO-Nexar and TiO_2-Nexar films. Results will include casting setup and procedure, initial film characterization, and initial bacterial testing with the cast films.

Modelling of Feed Flow in Ultrafiltration Channels Using Computational Fluids Dynamics – Effect of Spacer Geometry Design.

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In this study a laminar crossflow filtration in a rectangular channel was simulated using the computational fluid dynamics (CFD) software ANSYSFLUENT. CFD was used to solve Reynolds-averaged Navier-Stokes equations and to assess the impact of change in the surface shear, boundaries, and shear strain, thus effectively studying their influence on the membrane fouling phenomenon. A three-dimensional numerical solution of the Navier–Stokes equations were developed using the Finite volume method. Varied ultrafiltration channel spacer sizes of 0.1, 0.2, 0.4 micrometers were simulated. SAMPLE of solution control was used as a pressure-velocity coupling and QUICK for momentum discretization. Scaled residual monitors were decreased up to 10^{-5} for convergence satisfaction conditions. The larger spacers of 0.4 microns led to increased pressure drop across the membrane, as well as, increasing the hydrodynamics shear stress. However, the larger spacers of 0.4 microns led to the formation of localized stagnation or dead zones, where the membrane fouling phenomena may be increased. The influence of the feed spacer size on flow patterns inside the unltrafiltration unit will be discussed for each geometry at different feed flow rates in the range of 1 LPM to 7 LPM. The study demonstrated that the thickness of the ultrafiltration channel of 0.2 microns had the optimum results for the velocity and pressure profiles at different flow rates.

250 High Fouling Resistance Thin-Film Composite Membranes with Copolyazole Substrates for Osmotically Driven Processes.

Phuoc H.H. Duong[1]*, Stefan Chisca*[2]*, Peiying Hong*[3]*, Hong Cheng*[4]*, Suzana Nunes*[5]*, and Chung Tai-Shung*[6]
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MEXSY MemBrain TechnOntology: Portal and Analytic.

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MetaExpert Systems (MEXSY) – is a new class of expert systems for universal applications, including corporate information systems [1]. Starting since original meta-theoretical approach to formal synthesis of theories in physics and chemistry (1995-1997) [2-4] and having brilliant experience of the Invention Machine project (Boston, 1998-2001) [5], MEXSY technology opens a new opportunities for knowledge based applications in modern information space (master data, big data, social networks, semantic web, etc). Many large companies (including Fortune Global 500 list participants) use the MEXSY CorpBrain technology benefits in their real practice of data management (solutions: MEXSY MDM, MEXSY Expert, etc) [5-7]. Another (parallel) project of the MEXSY solutions development is the MEXSY MemBrain [8], which now also ready to go from research mode (2002-2011) [8] to real applications.

Experience of Invention Machine, Ontologic Classifier, and MEXSY projects allows to develop a new approach to accelerate development of technologies – MEXSY TechnOntology, or the MEXSY MemBrain TechnOntology in the case of membrane science and technology, which (the approach) may be organized as a memrane technology knowledge portal. This is a way to accumalate and use all knowledge about semipermeable membranes and membrane technologies. First version of the knowledge portal needs a knowledge base with simple navigation on the domaign information (books, journals, conferences, web-sites, etc). Next version of the portal should empowered by "domaign-oriented search engine" MEXSY Analytics, a part of MEXSY CorpBrain 2.0 (for enterprises) [1] or MEXSY WebBrain solution (for the industry, the MemBrain TechnOntology option). It's necessary to discuss some special questions about the membrane technology and portal with the professional community (for example North American Membrane Society) for better understanding (and formal presentation in the knowledge base) of real current problems of the industry. The milestone of the MEXSY TechnOntology project is the MEXSY MemBrain TechnOntology portal, as real accelerator for the membrane science and technology development. Then the experience of acceleration may be used in another industries (environment engineering, materials engineering, alternative energy, etc)

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Since 2010 Invention Machine is a part of IHS, and TechOptimizer & Cobrain are inside of IHS Goldfire solution, product of IHS:

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MEXSY MemBrain in Membrane Characterization.

Alex Seregin[1] *and* ***Jeff Zhuk***[2]
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MetaExpert Systems (MEXSY) – is a new class of expert systems for universal applications [1-2]. MEXSY MemBrain project studing MEXSY solutions in the field of membrane science and technology [3] is moving to real applications. So it’s necessary to discuss the actual MEXSY MemBrain knowledge base content with professional community (North American Membrane Society) for better understanding (and formal presentation in the knowledge base) of real current problems of the industry.

This presentation considers MEXSY MemBrain knowledge base in whole (membrane science and technology) and in part of membrane characterization [4] to develop related part of MEXSY MemBrain TechnOntology knowledge portal [1]. For another examples see [5-7].

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Comparative Analysis of Fouling Mechanisms in CTA and TFC Membranes.

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WATER TREATMENT, RECLAMATION & REUSE

251 Optimized Ultrafiltration Backwash with Real-Time Control of Coagulant Dosing.

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253 Removal of Organic Micro-Pollutants (phenol, aniline and nitrobenzene) Via Forward Osmosis (FO) Process: Evaluation of FO As an Alternative Method to Reverse Osmosis (RO).

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Onsite Treatment of Raw Produced Water through the Use of Forward and Reverse Osmosis.

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The U.S. Department of Energy (DOE) projects the production of oil and gas (O&G) to increase 48 and 56 percent by the year 2040, respectively, compared to 2012 production levels. Once a well has been developed, every barrel of oil produced will also generate roughly 9.2 barrels of produced water. Produced water is known to be saline, high in chemical oxygen demand (COD), and contain large concentrations of minerals, factors that pose a danger to human and environmental health if not disposed of properly. For these reasons the handling of produced water is a costly logistical challenge to transport, treat, or dispose of. The most common disposal practice is deep well injection of produced water; however, tighter regulations in the eastern U.S restricting deep well injection and unpredictable water resources create a need for a new onsite treatment process.

Forward osmosis (FO) coupled with reverse osmosis (RO) could provide high quality permeate capable for industrial and agricultural reuse, alleviating water tensions in arid regions and disposal logistic of raw produced water. Compared to current onsite treatment trains, the FO/RO system has exceptional product water quality due to a dual semipermeable membrane system, which has a 97 percent removal of a broad range of contaminants. This study focused on the long term performance of a pilot scale FO/RO system treating raw produced water from the O&G industry. The system consists of a 200 gallon FO Feed tank, 4.93 of FO membrane and 8.4 of RO membrane. The FO/RO system was operated at water recoveries of 0, 25, and 50 percent. The system performance was evaluated through the following parameters: specific flux, specific reverse salt flux, trace organic removal, and metal removal. The FO/RO system was operated continuously for periods of two weeks, during which the FO water flux decreased from 3.1 LMH to 1.8 LMH and produced 4,200 L of high quality permeate.

There are three potential factors that drive this decrease in water flux over time 1) The reverse salt flux increases the salinity of the feed water, therefore decreasing the osmotic driving force across the membrane 2) over time a fouling layer is developed on the FO membrane by the raw produced water, reducing water flux across the membrane, and 3) a decreasing water permeability coefficient due to chemical changes of the polymeric FO membrane. This value corresponds to the membranes physical composition, which should remain constant after the system stabilizes. Because this value never remains constant, it could be hypothesized that the produced water is interacting with the membrane surface, possibly altering the surface chemistry that facilitates water diffusion through the membrane. From these findings a standard operating procedures was developed, which optimizes backwashing intervals, minimizes decrease in water flux, and maintains a constant water permeability coefficient. These improvements will increase the viability of the FO/RO technology, possibly resulting in a commercial implementation.

Direct Contact Membrane Distillation (DCMD) for Industrial Wastewater Reuse: Managing the Accumulation of Organic Compounds in DCMD Product Water.

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Treating complex, highly saline industrial wastewaters, such as produced water from oil and gas extraction, is very costly, but direct contact membrane distillation (DCMD) is a novel process that can decrease water treatment costs. In DCMD, a heated feed stream is distilled at low–temperature (40-80°C) inside a membrane module and the distillate is collected in the permeate collection stream. While many researchers have shown that DCMD systems have high salt rejection, few studies have analyzed the rejection of organic compounds (OCs), which are present in many industrial wastewaters. The research outlined in this presentation indicates that due to the temperature gradient between the feed and permeate collection streams, volatile and semi-volatile compounds can accumulate in the permeate collection stream at higher concentrations than in the feed. As a result, the OC concentration in DCMD product water should be carefully monitored especially for applications with human exposure. To evaluate the accumulation of OCs in the DCMD product water, flux tests of synthetic wastewater (brine solutions containing industrially relevant OCs of varying volatility) were tested in a batch DCMD system. The water flux and concentration of OCs in the feed and permeate collection reservoirs were monitored over 5 hours. A Fickian mass transfer model was developed to fit the data and describe the change in reservoir concentration over time. This model can be used to predict whether the DCMD product water will meet the OC discharge requirements and determine if post-treatment is necessary.

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Volatile and Semi-Volatile Contaminant Transport in Direct Contact Membrane Distillation.

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Membrane distillation (MD) is a thermally driven separation process based on mass transport of water across a microporous, hydrophobic membrane. Transport is caused by a vapor pressure differential across the membrane that is generated by a thermal gradient. Recent advances in new membrane technologies and waste heat capture have made MD systems the subject of renewed interest as an alternative membrane technology for water treatment. Theory indicates that MD has high rejection rates for non-volatile compounds, such as ions and metals, and high permeability of volatile and semi-volatile compounds. The general assumption has been that this broad classification of volatile versus non-volatile is sufficient for determining the applicability of MD to a given source water, but little research has been done to examine the mechanics and physical phenomena of volatile contaminant transport in MD systems. Recent experimental data confirms that the earlier assumption was too broad, and that rejection of volatile and semi-volatile compounds vary significantly.

A novel, gas-tight direct contact membrane distillation system (DCMD) was designed and constructed to evaluate factors influencing transport of volatile and semi-volatile compounds in MD. The system retains volatile components, allowing for greater contaminant recovery and closure of the mass balance. Various contaminant classes, including metals, ionic salts, nitrogenous disinfection byproducts, volatile organic compounds (including phthalates, phenols, polyaromatic hydrocarbons, anilines, chlorinated aromatics, and amines), and pharmaceutical and personal care products were tested for transport in the system. These contaminant mixtures include diverse compounds with a very wide range of chemical properties, and spanned 10 orders of magnitude in air-water equilibrium partitioning (K_H). Rejection of the non-volatiles was generally above 99%, as expected, while the rejection of volatile compounds varied significantly. Membrane passage was compared to the physicochemical characteristics of each compound. Volatility, as assessed by K_H, weakly correlated with rejection, although there exist a number of compounds whose observed transport was inconsistent with their Henry's law constant. It was also found that many hydrophobic compounds (e.g., PAHs, large chlorinated aromatics, and phthalates) exhibited extensive sorption and hydrophobic partitioning to system components such as tubing, containers, and the membrane itself, suggesting that DCMD is not an appropriate treatment for these types of compounds. The results of this study are a major step towards our mechanistic understanding of the transport of compounds in DCMD based on their physicochemical properties.

Membrane Distillation for Treating Hydraulic Fracturing Flow Back Waters.

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Hydraulic fracturing flow back waters often exhibit very high TDS (in excess of 100,000 ppm). Treatment of these highly impaired wastewaters is a major challenge due to the presence of high TDS and organic contaminants. Pressure driven membrane processes such as reverse osmosis are impractical for treating very high salinity wastewaters due to the high osmotic back pressure that must be overcome. One of the technologies that is being investigated for treating these produced waters is membrane distillation.

Here we have screened a number of commercially available microporous hydrophobic membranes. We have characterized membrane surface as well as bulk properties. Using bulk membrane properties, we calculate a structural parameter that indicates membranes that should display the highest permeate flux. Permeate fluxes were determined for all membranes using a model feed stream containing a 20,000 ppm (0.34 M) NaCl. We have compared the observed permeate fluxes with values obtained for the structural parameter. Next membranes that displayed the highest permeate fluxes were challenged with feed streams containing 100,000 ppm (1.7 M) NaCl. The feeds stream was concentrated until the permeate flux rose quickly while the conductivity of the permeate increased rapidly above 50 mS cm^{-1} indicating the passage of the feed through the membrane pores. Finally, these membranes were tested with real produced waters. Our results indicate that a staged process using membranes with different bulk and surface properties is necessary to concentrate the feed to over 350,000 ppm. Further our results indicate the importance of membrane surface properties in order to prevent breakthrough of the feed.

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Overcoming Challenges in Fabrication of Thin Metallic Membranes for Nitrogen Separation.

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