

## ORAL PRESENTATIONS

**MONDAY 9:30 am** - Kings Garden 4

### **1a - Hydrodynamic-colloidal interactions of an oil droplet and a membrane surface**

Mariano Galvagno (Technion - Israel Institute of Technology), Guy Z Ramon (Technion - Israel Institute of Technology)\*

Membranes offer a superior separation capacity for stable emulsions, which are otherwise difficult to process. However, membrane fouling is always prevalent and requires extensive backwashing and cleaning as part of the operating regime. Oil droplets deform when in close proximity to a membrane, primarily due to permeation drag, which can lead to irreversible deposition on the membrane. Understanding the influence of hydrodynamic stresses and colloidal interactions between droplets and membranes will inform better engineered membrane surfaces and process conditions. Using a long-wave hydrodynamic description that incorporates wettability via a Derjaguin (disjoining) pressure and electrostatic repulsion via electric double layer (EDL) contributions, we derive a set of equations for the thickness and pressure in the liquid film separating the droplet and the permeable membrane. Numerical simulations are used to analyse equilibrium states where a zero net force acts on the droplet, to investigate the influence of droplet shape, distance from the membrane, membrane permeability and characteristic parameters of the colloidal interactions on the overall repulsion / attraction towards the membrane surface. A stability phase diagram is constructed in terms of the modified capillary number - accounting for the ratio of the viscous and surface tension forces - and a parameter representing the ratio of the hydrodynamic pressure scale over the electrostatic interaction intensity. These calculations are used to classify stable (upward deflection, increasing distance from the membrane) vs. unstable drop shapes (downward deflection bringing the droplet closer to the membrane), and investigate conditions leading to irreversible deposition onto the membrane. In particular, the model can describe how membrane properties and emulsion characteristics dictate a 'critical' flux.

**MONDAY 10:00 am** - Kings Garden 4

### **1b - Do Graphene Oxide Nanostructured Coatings Mitigate Bacterial Adhesion to Membrane Interfaces?**

Santiago Romero-Vargas Castrillon (University of Edinburgh)\*, Sara BinAhmed (University of Minnesota), Karl Wuolo-Journey (University of Minnesota)

Graphene oxide (GO) is a one-atom thick, two-dimensional sheet of hexagonally arranged carbon atoms, decorated with carboxyl, hydroxyl, and epoxide functional groups. GO nanosheets possess exceptional physical and chemical properties, as well as antimicrobial activity against both gram-negative and -positive bacteria, rendering them a promising building block for anti-biofouling coatings. Extensive research has been performed to explore the mechanisms underlying GO's biocidal activity. Yet, to date, a fundamental understanding of the behavior of bacterial cells at GO-functionalized aqueous interfaces is largely lacking. Elucidation of the interfacial activity of GO is essential for the development of graphene-based environmental applications, such as membrane materials for water purification. In this study, we use single-cell force spectroscopy to investigate the mechanism of microbial adhesion of single *P. fluorescens* cells to polyethersulfone ultrafiltration (UF) membranes. We find that, in addition to possessing antimicrobial activity, GO nanostructured coatings result in a statistically significant decrease in the bioadhesion forces compared to GO-free control UF membranes. Given that GO does not significantly modify the hydrophilicity or zeta potential of the UF membrane surfaces, we speculate that GO mitigates bioadhesion due to steric repulsion, i.e., through a mechanism akin to that of antifouling polymer brushes. This investigation therefore provides insight into GO's properties at biological interfaces, and provides novel nanoscale insights into its antifouling functionality.

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**1c - Fouling mechanisms in constant flux crossflow ultrafiltration**

Alon Kirschner (The University of Texas at Austin)\*, Yu-Heng Cheng (The University of Texas at Austin), Donald Paul (The University of Texas at Austin), Robert Field (University of Oxford), Benny Freeman (The University of Texas at Austin)

Four fouling models due to Hermia (complete pore blocking, intermediate pore blocking, cake filtration and standard pore blocking), have long been used to describe membrane filtration and fouling in constant transmembrane pressure operation of membranes. A few studies apply these models to constant flux dead-end filtration systems. However, these models have not been reported for constant flux crossflow filtration, despite the frequent use of this mode of membrane operation in practical applications. We report derivation of these models for constant flux crossflow filtration. Of the four models, complete pore blocking and standard pore blocking were deemed inapplicable due to contradicting assumptions and relevance, respectively. Constant flux crossflow fouling experiments of dilute latex bead suspensions and soybean oil emulsions were conducted on commercial poly (ether sulfone) flat sheet ultrafiltration membranes to explore the models' abilities to describe such data. A model combining intermediate pore blocking and cake filtration appeared to give the best agreement with the experimental data. Below the threshold flux, both the intermediate pore blocking model and the combined model fit the data well. As permeate flux approached and passed the threshold flux, the combined model was required for accurate fits. Based on this observation, a physical interpretation of the threshold flux is proposed: the threshold flux is the flux below which cake buildup is negligible and above which cake filtration becomes the dominant fouling mechanism.

**MONDAY 11:00 am** - Kings Garden 4

**1d - Fouling-Resistant, Multi-Functional Membranes with Ultra-Thin Hydrogel Selective Layers using Interfacially Initiated Free Radical Polymerization (IIFRP)**

Ayse Asatekin (Tufts University)\*, Ilin Sadeghi (Tufts University), Eric Liu (Tufts University), Alice Oliveira Aguiar (Tufts University), Hyunmin Yi (Tufts University)

Hydrogels are promising materials as membrane selective layers due to their fouling-resistance, tunability, and functionalizability. Yet, the fabrication of thin, uniform hydrogel membrane selective layers using a simple, scalable process is a challenge. We developed a novel method, interfacially initiated free radical polymerization (IIFRP), for the fabrication of ultra-thin hydrogel selective layers on porous supports in a simple and reproducible process. This method utilizes the segregation of the monomer and the photoinitiator into two separate, immiscible phases to form a very thin, uniform and defect-free hydrogel layer at the interface upon photopolymerization. The resulting hydrogel-coated membranes have selective layers as thin as <100 nm, and can separate the proteins based on size. The method is readily tunable for a broader range of separations by altering experimental parameters or the addition of inert porogens or comonomers. IIFRP can also be used to prepare membranes that simultaneously remove large organic molecules and catalytically treat smaller contaminants by incorporating catalytic nanoparticles (NPs) into the membrane selective layer. We prepared hybrid water filtration membranes incorporating catalytic NPs immobilized on tobacco mosaic virus (TMV) nanotemplates within their ultrathin hydrogel selective layers by adding the TMV-templated NPs to the monomer solution during IIFRP. These membranes catalytically reduce Cr(VI), a toxic and carcinogenic contaminant, to non-toxic Cr(III), achieving up to 98% conversion in a single pass. Catalytic activity is fully retained with continuous filtration for at least 3 days. These results illustrate a versatile approach for integration of various nanomaterials within membrane selective layers, enabling the creation of advanced membranes with new and versatile functionalities for next-generation applications.

**MONDAY 11:30 am** - Kings Garden 4

**1e - Unravel the Gordian Knot of membrane desalination: Understanding and mitigating silica scaling in reverse osmosis**

Tiezheng Tong (Colorado State University)\*, Song Zhao (Tianjin University), Amanda Quay (Carnegie Mellon University), Yunlong Qi (Tianjin University)

Mineral scaling, a largely unexplored problem compared to organic and biological fouling, significantly constrains water recovery of membrane desalination. Silica scaling is among the most challenging types of scaling due to the complex nature of scaling mechanisms and the lack of effective anti-scalants. In this presentation, we will present our research on understanding the mechanisms as well as developing novel scaling-resistant membranes associated with silica scaling in reverse osmosis (RO). First, surface properties of thin-film composite (TFC) polyamide membranes were correlated with silica scaling in RO desalination. By developing a battery of ten membranes grafted with a variety of polymers, we were able to demonstrate a strong correlation of membrane surface charge with the extent of silica scaling, which was independent of both membrane hydrophilicity and surface energy. A more negative surface charge reduced silica scaling, suggesting the important role of negatively charged silica species in scale formation. Further, we investigated combined silica scaling and protein fouling. Our results showed that water flux decline was synergistically enhanced when silica and protein coexisted in the feedwater. The silica-protein interactions were elucidated by using a series of microscopic and spectroscopic analytical tools, which revealed a facilitating effect of proteins in the formation of aggregates with silica. Lastly, a novel TFC polyamide membrane modified with layer-by-layer (LbL) assembly was developed to improve resistance to combined silica scaling and protein fouling. Our systematic work provides fundamental insights into the mechanisms governing silica scaling in RO, and highlights the potential of membrane surface modification as a strategy to reduce silica scaling and improve RO water recovery.

**MONDAY 12:00 pm** - Kings Garden 4

**1f - RO Mineral Scale Mitigation via Self-Adaptive Feed-Flow Reversal**

Yeunha Kim (UCLA)\*, Anditya Rahardianto (UCLA), Tae Lee (UCLA), Yoram Cohen (UCLA)

Reverse osmosis (RO) membrane desalination is increasingly used for production of potable water from seawater and brackish water and in municipal and industrial water reuse applications. However, RO processes are adversely impacted by membrane mineral scaling especially at high recovery. Membrane surface scaling decreases membrane water permeability, increase operating cost and reduce membrane longevity. Membrane scaling has been partially mitigated via antiscalant dosing of the RO feed, but this is at an added cost. An alternate approach to scale mitigation can be achieved via RO Feed flow reversal (FFR) which is a chemical-free method. By periodically reversing the direction of the raw RO feed, mineral scale that developed at the membrane stage exit can be removed via dissolution and the membrane permeability is recovered. An evaluation of the FFR process in a spiral-wound RO pilot system was undertaken whereby flow reversal was triggered by a novel membrane scale monitoring (MSM) system. The RO pilot was fitted with an arrangement of automated valves and piping for self-adaptive automated switching of the feed flow direction. The MSM system contains a membrane channel that mimics the level of concentration polarization of the spiral-wound RO element being monitored. Studies with gypsum as a model scalant demonstrated that continuous RO desalination was feasible without scaling and without antiscalant dosing up to twice the saturation limit of gypsum.

**MONDAY 9:30 am** - Ballroom 3

**2a - Continuous on-demand dehydration of solvents in flow chemistry manufacturing processes**

Hannah Murnen (Compact Membrane Systems)\*, Sudip Majumdar (Compact Membrane Systems)

Anhydrous solvents can be critical in the development and production of new pharmaceutical molecules, affecting yield, product quality and process efficiency to name just a few key elements. Production and management of those anhydrous solvents is not always trivial given the temperature, quality and process requirements of APIs, particularly in flow chemistry systems. Membrane dehydration and purification can provide an avenue for efficient and cost-effective, on-demand production of these anhydrous solvents. Compact Membrane Systems has installed several fluoropolymer membrane pervaporation systems into flow chemistry manufacturing processes to allow inline dehydration of solvents. One example of this work was published in OPR&D along with authors from Pfizer and Asymchem and provides a new route to manage solvents in flow chemistry processes. This presentation will discuss solvent purification and management in flow chemistry processes using pervaporation membranes and will also cover specific operational issues such as how to manage low flow rates or small hold up volumes.

**MONDAY 10:00 am** - Ballroom 3

**2b - How membrane technology has been successfully applied to ethanol processing**

Stephan Blum (Whitefox Technologies)\*, Trond Heggenhougen (Whitefox Technologies), Meridith K Bridge (Whitefox Technologies)

Whitefox's Integrated Cartridge Efficiency (ICE) is a membrane-based dehydration technology that removes bottlenecks in biofuels processes. The ICE solution dehydrates water-rich recycle streams that significantly reduces the load on existing equipment and frees up capacity in distillation and dehydration sections, enabling producers to increase ethanol output and revenues, as well as improve margins by reducing energy costs, improve carbon intensity (CI) scores, reduce cooling water costs year-round, and reduce operation and maintenance costs. Existing plants use Molecular Sieve Units (MSU) to dehydrate ethanol. Recycle streams generated during distillation and MSU dehydration create bottlenecks and limit plant expansion. These regenerate streams are therefore recycled to distillation that increases load and energy consumption in the distillation columns. The ICE solution is a stand-alone membrane system that removes existing bottlenecks by dehydrating water-rich recycle streams (up to 50 wt%) to target moisture in one pass. This significantly reduces the load on distillation columns and MSU allowing for plant expansion, energy and cooling water savings. Whitefox is currently installed at four U.S. plants with several more installations planned for 2019. Benefits seen from an ICE installation include: load reduction on rectifier/side stripper and molecular sieves, removal of fluctuation in columns, reduction in steam and improved Carbon Intensity levels, reduction in cooling water recirculation rate and electrical load. Whitefox will share information about its vapor permeation membranes, module configurations and process diagrams before and after an ICE installation. Whitefox will also take the audience through the customer journey from baselining to complete installation, demonstrating the savings by providing operating data from its existing U.S. installations to show tangible benefits that can contribute to profitable operations.

**MONDAY 10:30 am** - Ballroom 3

**2c - Modeling the effect of different single-walled carbon nanotube orientations on permeation through mixed matrix membranes**

Ali Zamani (University of Ottawa)\*, Jules Thibault (University of Ottawa), Handan Tezel (University of Ottawa)

Pervaporation, a membrane-based process, is considered to be a promising technique for the separation of organic compounds from aqueous solutions. Different types of polymeric membranes have been used for this process due to their wide range of separation properties, but these types of membranes are suffering from the trade-off between permeability and selectivity. Mixed matrix membranes (MMMs), comprising an inorganic filler phase embedded into a polymer matrix, have emerged in an attempt to partly overcome some limitations of conventional polymer and inorganic membranes. Among them, membranes incorporating single walled carbon nanotubes (SWCNTs) having the potential for transcending Robeson's upper bound. Recent studies tried to align SWCNTs in the host polymer matrix and results showed an improvement in membrane permeability. However, while much effort has been devoted to SWCNTs mixed matrix membrane in practice, their modeling is mostly based on early theories for transport in composites. These theories consider ideal morphology, which is very challenging to reach because of the imperfect filler-polymer adhesion. Also, they neglect the orientation of the nanotubes. Therefore, models for the permeability in MMMs often do not perform well when compared to experimental permeation data. These non-idealities can be classified into the following three major categories: (i) interface voids, (ii) rigidified polymer layer around the fillers, and (iii) particle pore blockage. Therefore, non-ideal morphology for three-phase systems containing filler-polymer interface defects, while considering SWCNTs orientation has been proposed. The Fickian diffusion equation was used to calculate the concentration profile of the component through the block of the mixed matrix membrane. Simulations showed that the membrane performance is highly dependent on the filler orientation and MMMs effective permeability would be increased up to 35% by aligning the SWCNTs vertical to the surface.

**MONDAY 11:00 am** - Ballroom 3

**2d - Unique 3D printed spacers for process enhancement in membrane distillation**

Navya Thomas (Khalifa University)\*, Nurshaun Sreedhar (Khalifa University), Oraib Al-Ketan (Khalifa University), Reza Rowshan (New York University Abu Dhabi), Rashid Abu Al-Rub (Khalifa University), Hassan Arafat (Khalifa University)

Spacers, an essential component of an effective module design, influence the hydrodynamics in the flow channels of membrane distillation (MD) units, thus inducing multifaceted impact on the process performance. In this study, we investigated the performance of innovative 3D printed spacer designs based on mathematically modelled triply periodic minimal surfaces (TPMS), which was benchmarked against a conventional commercial mesh spacer (CS). The TPMS structures are particularly interesting because of their interconnected maze-like tortuous pathways that creates increased turbulence, and zero mean curvature that abates dead zone formation. Performance evaluation was based on flux and flux stability, heat transfer, feed channel pressure drop and fouling. Several TPMS architectures were evaluated, including Schwarz CLP, tCLP, P; Schoen Gyroid and Fisher Koch S surface. The best performing TPMS spacer design, the tCLP, resulted in flux and overall film heat transfer coefficient enhancement of 60% and 63%, respectively, compared to the CS in direct contact MD. The improved performance was further elucidated through temperature polarization modelling. However, the tCLP spacer also exhibited higher channel pressure drop compared to CS. For further improvement, a hybrid spacer design which combines two TPMS architectures was conceived, and resulted in high flux, on par with tCLP, but at a lower pressure drop penalty. Under fouling inducing conditions, processing RO brine with continuous feed concentration build-up (75,000-100,000 ppm), the use of TPMS spacers resulted in significant flux stabilization over time, as compared to CS. Additionally, inorganic scaling tests using calcium sulfate as the feed solution were conducted and a new technique for scale mapping using alizarin red S staining was used. The latter technique showed that membrane areas in contact with CS had a two-fold higher scalant deposition than those in contact with the TPMS spacers.

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**2e - 2D boron nitride encapsulated nanofiber membranes for membrane distillation**

Yunchul Woo (Korea Institute of Civil Engineering and Building Technology)\*, Ho Kyong Shon (University of Technology Sydney), June-Seok Choi (Korea Institute of Civil Engineering and Building Technology)

The instability of PVDF membranes in membrane distillation (MD) for seawater desalination still remains a problem awaiting solution, despite tremendous efforts. Here we propose simple and feasible approach for improving desalination performance through incorporation of two-dimensional boron nitride nanosheets (BNNSs) in PVDF-co-HFP electrospun nanofiber membrane (BNs-PH) as well as demonstrate its origin for fundamental understanding. The BNs-PH membrane exhibits stable water vapor flux (18 LMH) and superior salt rejection (99.99%), even after operation for 280 h (Commercial PVDF: steep decay within 28 h, and neat PH: wetting within 4h). From structural/chemical analysis, the BNNSs play a crucial role in forming favorable phase of the PH polymer crystal structure, inducing superhydrophobic surface with the larger nanoporosity and higher heterogeneity as well as enhanced mechanical properties for long-term operation. Furthermore, theoretical modelling for air gap MD (AGMD) system is clearly consistent with the experimental data. Approach introduced in this study has great potential for broad application with other desalination system, which will boost various water treatment applications.

**MONDAY 12:00 pm** - Ballroom 3

**2f - Impact of membrane properties on scaling-induced wetting in membrane distillation**

Allyson L McGaughey (University of Southern California)\*, Prathamesh Karandikar (University of Southern California), Malancha Gupta (University of Southern California), Amy Childress (University of Southern California)

Membrane distillation (MD) relies on a hydrophobic, unwetted membrane to reject solutes. However, at high salinities, salt precipitation (scaling) on the membrane can induce pore wetting. Implicit assumptions are often made about pore wetting: that feed-side hydrophobicity and pore size (and feed stream properties) control wetting. Neither the role of asymmetric nor internal membrane properties in maintaining membrane hydrophobicity have been studied. In this study, we utilized initiated chemical vapor deposition to deposit a hydrophobic polymer (pPFDA) on a hydrophilic substrate (CA), resulting in symmetric superhydrophobicity ( $161^\circ$  average contact angle on both sides of membrane) without impacting porosity. However, when pPFDA was deposited on a hydrophobic substrate (PTFE), hydrophobicity was unchanged and an asymmetric, low-porosity (5%) surface layer formed - likely due to low surface energy of PTFE preventing spreading. In short-term performance with scaling, both materials behaved similarly with high wetting resistance. However, in longer-term testing, the superhydrophobic pPFDA-CA membrane wetted much faster than the low-porosity pPFDA-PTFE membrane. Superhydrophobic membranes are frequently used in MD for their wetting resistance; they have also been suggested as anti-scaling materials. Because the energy barrier to crystal nucleation ( $\Delta G_M$ ) increases with contact angle, superhydrophobicity is expected to reduce scaling. However, despite the higher  $\Delta G_M$  of the superhydrophobic membrane, nucleation eventually occurred and wetting followed. The low surface porosity membrane provided a more robust barrier. The reduced pore size may have prevented crystal growth into pores by size exclusion. Also, internal hydrophobicity (PTFE pore walls) may have inhibited liquid progression. In ongoing work, we are investigating surfactant-induced wetting; results will be presented.

**MONDAY 9:30 am** - Kings Garden 3

**3a - Sacrificial Protective Layer for Fouling Control in Reverse Osmosis Desalination**

Moon Son (Penn State University)\*, Wulin Yang (Penn State University), Szilard S. Bucs (King Abdullah University of Science and Technology), Maria F. Nava-Ocampo (King Abdullah University of Science and Technology), Johannes S. Vrouwenvelder (King Abdullah University of Science and Technology), Bruce E. Logan (Penn State University)

A new approach was examined to minimize inevitable membrane fouling in reverse osmosis (RO) desalination based on adding a sacrificial coating of a protective layer (PL) using two polyelectrolytes, poly(diallyldimethylammonium chloride) and poly(sodium-4-styrenesulfonate), to the membrane surface. After the PL is fouled, this coating was removed by flushing with a highly saline solution such as an RO brine, and a new coating was regenerated in situ to provide a fresh PL coating on the membrane surface. The utility of this approach was demonstrated by conducting four consecutive dead-end filtration experiments using a model foulant (alginate, 200 ppm) in a synthetic brackish water (2000 ppm of NaCl). Brine removal and regeneration of the PL coating restored the water flux to an average of  $97 \pm 3\%$  of its initial flux, compared to only  $83 \pm 3\%$  for the pristine membrane. The average water flux for the PL-coated membranes was  $15.5 \pm 0.6 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  until the flux was decreased by 10% versus its initial flux, compared to  $13.4 \pm 0.5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  for the non-treated control. Applicability and stability of the PL coating under cross-flow conditions was also further examined. These results suggest that the use of a sacrificial PL coating could provide a more sustainable approach for addressing RO membrane fouling. In addition, this approach could be also applied on other surfaces such as feed spacers, reservoirs, and pipes and released as needed to help remove biofilms or accumulated organic matter.

**MONDAY 10:00 am** - Kings Garden 3

**3b - Water Transport through Ultrathin Polyamide Nanofilms Used for Reverse Osmosis**

Zhiwei Jiang (Imperial College London)\*, Santanu Karan (Imperial College London), Andrew Livingston (Imperial College London)

Thin film composite membranes comprising polyamide films as separating layers have been widely used in reverse osmosis (RO) applications for decades. These membranes have become the most attractive option for desalination due to the energy efficiency of reverse osmosis compared to other separation techniques such as multiple effect evaporation. Conventionally, polyamide films are fabricated via interfacial polymerisation (IP) between m-phenylenediamine (MPD) in an aqueous phase and trimesoyl chloride (TMC) in an organic phase on an ultrafiltration support. This results in the formation of crumpled polyamide films with apparent thickness in the range of ~50 to 300 nm. Such crumpled features created on ultrafiltration supports present a challenge to investigation of the active thickness of the polyamide layer and to understanding of the transport mechanism through the membranes. To tackle this challenge, herein we report ultrathin polyamide films (down to ~6 nm) fabricated at a free liquid-liquid interface, independently from any support materials. Polymerisation at a free interface created ultrathin free-standing polyamide nanofilms which could be transferred independently onto various supports. Interestingly, the pristine support with fast water transport exhibited >4 times higher permeance of the resulting composite membrane while identical nanofilms were attached on. In addition, by controlling the interfacial reaction conditions, we manipulated the intrinsic thickness of polyamide nanofilms down to ~6 nm. Composite membranes comprising such smooth films showed comparable water permeances ( $2.7 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ ) to commercial and reported RO membranes with crumpled features. Considering that the ultra-smooth surfaces of the polyamide films provide less than one quarter of the permeable area of that provided by crumpled features, the water permeance per area of nanofilm is more than four times higher than for conventional RO membranes.

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**3c - Balancing Carbon, Nitrogen and Phosphorus Concentration in Seawater as a Strategy to Prevent Accelerated Membrane Biofouling**

Siqian (Simon) Huang (University of Minnesota, Duluth), Nikolay Voutchkov (Water Globe Consultants, LLC), Sunny Jiang (UC Irvine)\*

Membrane biofouling remains a significant challenge in seawater reverse osmosis desalination for drinking water production. This study investigated nutrient imbalance as the cause of biofouling in lab scale experiments and carried out a year-long field-testing at a seawater desalination pilot plant. Lab experiments showed that growth medium with excess organic carbon (C) but low nitrogen (N) and phosphorus (P) accelerated the production of bacterial biofilm. Balancing C to N and P ratio by adding N and P to growth medium increased the cell proliferation but reduced biofilm production. The cell excretion of excess C in the form of extracellular polysaccharides (EPS) was considered as a strategy for nutrient storage for future use. Cell enzyme activity assays indicated some of the bacteria had enhanced enzyme activity to degrade polysaccharides in the absence of organic carbon in growth medium, possibly using EPS in the biofilm. But others do not show enhanced enzyme activity. A year-long field study indicated that accelerated biofouling of membrane was associated with the elevation of total organic carbon (TOC) in the intake water. Dosing of intake stream with addition of N and P to balance the increase of TOC resulted in reduction of membrane biofouling. Microbial community analysis of the biofouling layer using 16s rRNA gene sequencing indicated biofouling communities varied with seasonal changes. Dosing of N and P did not induced dramatic changes in fouling community recovered from membrane surface. The outcomes of this work imply that accelerated membrane biofouling associated with elevated TOC in intake water is likely due to imbalance of C:N:P. Addition of N and P to rebalance the nutrients can alleviate the accelerate biofouling.

**MONDAY 11:00 am** - Kings Garden 3

**3d - Flow Reversal for Increased Recovery of 2nd Pass Seawater RO**

Tomer Osman (Rotec Water Ltd.), Dan Peled (AST-Water Ltd.), Noam Perlmutter (Rotec Water Ltd.), Arina Shulman (Mekorot Water Company), Riki Harpness (Mekorot Water Company), Sivan Bleich (Mekorot Water Company), Eli Korin (Ben-Gurion University), Jack Gilron (Ben-Gurion University)\*

A partial 2nd pass is needed on SWRO permeate when strict boron limits are imposed for agricultural needs. The pH of the 2nd pass feed is increased above pH=10 to maximize boron rejection, since Mg<sup>2+</sup> and Ca<sup>2+</sup> levels are quite low in the SWRO 1st pass permeate. The drive to reach maximum recovery from 1ST PASS permeate means that at recoveries above 90-92% become Mg<sup>2+</sup> concentrations are high enough to create large supersaturations of magnesium hydroxide (brucite) which can foul the membrane. The flow reversal technique invented by BGU scientists periodically switches the position of the last membrane element in the train with the first membrane element in the train so that the tail element which saw the most supersaturated conditions will now see the least supersaturated conditions of the feed element thus preventing onset of scaling. A planned expansion by Mekorot of the SWRO Sabha C plant near Eilat requires expanding the second pass as well to keep boron levels low. The feasibility of incorporating flow reversal into this expansion was evaluated in a pilot experiment using feeds and rejects from the existing second pass LPRO plant. To simulate a 4 stage second pass operation, Rotec implemented a pilot including four pressure vessels (PV) of four 4-inch elements divided into a 1st stage block with three pressure vessels in parallel and a 4th stage block with one pressure vessel. The feed blocks were fed by the feed to the existing second pass unit. The 4th stage block was fed by the concentrate leaving the existing three-stage second pass unit. The block in the 4th stage was periodically switched with a 1st stage PV while flipping the feed and concentrate connections. Non-increase of the axial pressure drops in the 4th stage were used as an online indicator of scale free operation. During pilot operation recoveries were increased to 97% and then to 98% for the final month with no sign of brucite precipitation.

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**3e - Zwitterionic poly(arylene ether sulfone) (PAES) copolymer for biofouling/chlorine resistant desalination membranes**

Yi Yang (Arizona State University)\*, Matthew Green (Arizona State University)

Amphiphilic poly(arylene ether sulfone)s with covalently bonded sulfobetaine groups (PAES-co-SBAES) show great potential for sea water desalination membranes. This family of polymers showed impressive performances on transport properties, bio-fouling/chlorine resistance and strong mechanical stabilities. Here we demonstrated a novel synthesis method to prepare the controlled zwitterionic charge content PAES polymers. The polymer chemical structures were analyzed by <sup>1</sup>H NMR spectroscopy and the molecular weight of polymers was identified by size exclusion chromatography (SEC). Our study indicated that with the introduction of zwitterionic charge in a rigid PAES matrix, the water permeance and antifouling ability were both remarkably improved to 2.5 L·m<sup>-2</sup>·h<sup>-1</sup>·bar<sup>-1</sup> and 94% of flux recovery ratio, respectively, while salt rejection remained at a high level (98%) even under the high exposure to chlorine (12,000 ppm·h). Specifically, the zwitterion functionalized free-standing PAES membranes were fabricated via the non-solvent induced phase separation (NIPS) with incorporation of solvent evaporation process. The membrane composition, surface morphology (roughness), cross-section morphology, and surface hydrophilicity were determined by fourier transform infrared (FT-IR) spectrum, atomic force microscopy (AFM), scanning electron microscopy (SEM), and water contact angle measurements, respectively. The results indicated that both the porosity of the support layer and surface hydrophilicity increased drastically due to the incorporation of hydrophilic SBAES segments. This work provided a valuable and scalable strategy to fabricate free-standing and bio-fouling/chlorine resistant desalination membranes, and further performance optimization and fundamental understandings on water/salt transport behaviors in this family of polymers are under investigation.

**MONDAY 12:00 pm** - Kings Garden 3

**3f - Chlorine resistance of functionalized HNTs-based TFN membranes**

Farhad Asempour (University of Ottawa), Somaye Akbari (Amirkabir University of Technology), Du Bai (University of Ottawa), Ramzi Aoun (University of Ottawa), Sofia Reyes Lombardo (University of Ottawa), Amirsajad Atashgar (University of Ottawa), Boguslaw Kruczek (University of Ottawa)\*

Thin Film Nanocomposite (TFN) Reverse Osmosis (RO) membranes are reported to have promising improvements compared to conventional Thin Film Composite (TFC) membranes in terms of separation characteristics for desalination. In this work, we investigate enhancing TFN membrane's stability and chlorine resistance by focusing on the functionalization of nanoparticles. Fully aromatic RO membranes were synthesized by in situ interfacial polymerization of TMC and MPD; Halloysite NanoTubes (HNTs) were used as the additive nanoparticles. The HNTs were functionalized by three different generations of amine terminated poly(amidoamine) PAMAM dendrimers. Resulting membranes, were treated by passive batch chlorination using 50 ppm NaOCl solution for 24 hr of exposure time. Physicochemical properties of modified HNTs and membranes were characterized by SEM, FTIR and water contact angle measurements. The water permeability and salt rejection of the membranes were evaluated by cross-flow RO experiments with brackish water. FTIR analysis revealed formation of amide bonds between dendrimers from functionalized HNTs with TMC monomer. The exposure to batch chlorination of both the reference TFC membrane and the modified HNT-based TFN membrane led to a decrease in salt rejection and an increase in the water flux. However, the respective changes in the performance of TFN membrane were smaller than those in the reference TFC membrane. Therefore, increasing the number of amine groups by increasing the generation of PAMAM dendrimers on HNTs improves chlorine resistance of the resulting TFN membrane.

**MONDAY 9:30 am** - Ballroom 4

**4a - Enantioselective Polymeric Membrane for Chiral Separation of Enantiomers**

Marine Michel (Imperial College London)\*

Chiral separation of enantiomers (optical isomers) is attracting interest as the demand for enantiopure pharmaceuticals is growing dramatically. Many pharmaceuticals exist as a mixture of two enantiomers which can present different biological response such as toxicological behaviour, therapeutic activity, or immune response. As they have the same physico-chemical properties, their separation is a challenging task but it is crucial as the incorrect enantiomer of the drug can offer no curative effect or even be detrimental. Optical resolution of racemic mixtures has been broadly studied by various methods including chromatography, preferential crystallization or membrane processes. The latest is seen as serious candidate to established chiral separation technologies, especially since it requires lower energy costs, is continuous, eco-friendly and easy to scale up. In optical resolution, the membrane acts as a selective barrier and transports one of the paired enantiomers preferentially because of a stereo-specific interaction between enantiomers and chiral recognition sites present in the membrane. Most studies have been performed using dialysis method, where the driving force is the concentration difference between feed and permeate. With this method the concentration of the final product is more dilute than that of the feed solution, and permeation is extremely slow. This work focuses on membrane-based enantioseparation technique, performed in pressure driven separation mode, which has the potential for large-scale production of enantiopure compounds and could pave the way for many more commercial applications satisfying the considerable demand for large-scale chiral separation techniques.

**MONDAY 10:00 am** - Ballroom 4

**4b - Tailored Synthesis of Inorganic-supported Polymer, Graphene, and Nanocomposite Membranes for Liquid-phase Separations**

Michael Z Hu (Oak Ridge National Laboratory)\*

Molecular separations of liquid mixture solutions represent a separation challenge that demands the nanoscale control of materials structures and tailoring of surface/interfacial functionality chemistry. Synthesis capability of nanostructured functional materials is foundational to advance separation membranes with better flux and selectivity. For biomass conversion to biofuel/biochemical processing, recovery of biooil and water-soluble oxygenated hydrocarbon molecules is critical to ensuring the carbon efficiency and bioeconomy. In this work, surface-engineered (superhydrophobic) nanoporous inorganic membranes were developed to provide several orders of magnitude higher flux in phase separation biooil-water emulsions. Ceramic tube-supported polymer membranes were developed to dewater and concentrate the aqueous solutions that contain oxygenated hydrocarbon molecules (such as carboxylic acid). Thin film nanocomposite membranes that contain embedded nanoparticles (such as graphene oxide or covalent organic frameworks) are also discussed for their promise in dewatering, desalination, and organic solvent separation.

**MONDAY 10:30 am** - Ballroom 4

**4c - Two-Dimensional (2D) Covalent Organic Framework Mixed-Matrix Membranes**

Phuoc Duong (University of Wyoming), Valerie Kuehl (University of Wyoming), Bruce Mastorovich (University of Wyoming), John Hoberg (University of Wyoming), Bruce Parkinson (University of Wyoming), Katie D Li-Oakey (University of Wyoming)\*

Mixed-matrix ultrafiltration (UF) membranes containing a new two-dimensional (2D) carboxyl-functionalized covalent organic framework (COF) as a nanofiller and polyacrylonitrile (PAN) as a polymer matrix have been investigated. The effect of COF concentration has been evaluated on the membrane morphology, intrinsic and mechanical properties, separation performance, and fouling propensity. Increasing COF concentration from 0 to 0.8 wt% could significantly enhance the rejection rate from 3.5 to 81.9 wt% for bovine serum albumin (BSA) and 65.0 to 99.4 wt% for gamma-globulin. Moreover, membrane hydrophilicity greatly increased, with the decrease of water contact angle from 64.4° to 45.3°. Overall, compared to the pristine PAN membrane, the mixed-matrix PAN membrane with 0.8 wt% COF demonstrated high water flux of 940 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>, advantageous protein retention (81.9% for BSA and 99.4% gamma-globulin), enhanced thermal stability, mechanical properties, and fouling resistance.

**MONDAY 11:00 am** - Ballroom 4

**4d - Enhancing water permeance in reduced graphene oxide membranes by chemical etching**

Xiaoyi Chen (The State University of New York at Buffalo)\*, Liang Huang (The State University of New York at Buffalo), Zhihao Feng (The State University of New York at Buffalo), Janavi Gohil (The State University of New York at Buffalo), Haiqing Lin (The State University of New York at Buffalo)

Reduced-graphene oxide (r-GO) membranes have emerged as a potential candidate for next-generation nanofiltration (NF) applications. However, previously reported r-GO membranes have lower water permeance than polyamide-based NF membranes because of the small 2D channels required to achieve good size-sieving ability. We report here an effective approach in enhancing the water permeance by creating nano-pores on the r-GO nanosheets. Specifically, GO sheets are chemically etched using H<sub>2</sub>O<sub>2</sub> to form holey GO sheets, which are then deposited on porous supports before being reduced by HI. The prepared membranes were thoroughly characterized using SEM, Raman Spectroscopy, FTIR, and XRD. The effect of the etching and reduction conditions on the membrane performance is systematically investigated. Increasing the etching time increases the water permeance with slight decrease in the salt rejection rate, while increasing the reduction degree decreases the water permeance and increases the salt rejection. For instance, increasing the etching time from 0 h to 4 h improves the water permeance from 0.4 L m<sup>-2</sup>·h<sup>-1</sup>·bar<sup>-1</sup> to 6.6 L m<sup>-2</sup>·h<sup>-1</sup>·bar<sup>-1</sup> by over 15 times, while the Na<sub>2</sub>SO<sub>4</sub> rejection remains at 98.5%. The r-HGO membranes exhibit NF performance comparable with the commercial polyamide-based membranes. For instance, when r-HGO with 4 h etching and a reduction using 34 wt% HI was fabricated into a 20 nm-thick membrane, it exhibits water permeance of 12 L m<sup>-2</sup>·h<sup>-1</sup>·bar<sup>-1</sup> and Na<sub>2</sub>SO<sub>4</sub> rejection of 91.4% at 4 bar and 22°C. We have also prepared multi-layer r-HGO membranes with various degrees of etching and evaluated for NF applications. We will also present the long-term stability test results of these membranes using a crossflow system.

**MONDAY 11:30 am** - Ballroom 4

**4e - Nanocomposite RO Membranes with High Aspect Ratio Functional Nanoparticles for Controlled Interfacial Transport**

Stephen M Martin (Virginia Tech)\*, Ethan Smith (Virginia Tech), E. Johan Foster (Virginia Tech), Keith Hendren (Virginia Tech), James Haag (Virginia Tech)

Thin film nanocomposite membranes (TFNs) are a recent class of materials that use nanoparticles to provide improvements over traditional thin film composite (TFC) reverse osmosis membranes. Prior work in our lab has demonstrated that significant improvements in flux can be achieved through the inclusion of functionalized carbon nanotubes (CNT) in the polyamide selective layer. We hypothesized that the rapid water transport occurs not in the internal pore of the CNT, but at the interface between the CNTs and PA matrix. Thus, careful control of surface functionality and polymerization conditions can be used to tune the membrane performance. In this study, TFNs were produced using high aspect ratio cellulose nanocrystals (CNCs) and TEMPO-oxidized cellulose nanocrystals (TOCNs) as nanoparticle additives. CNCs are broadly interesting due to their low cost, sustainability, and potential for surface modification. Two methods of membrane fabrication were used in order to study the effects of nanoparticle dispersion on membrane flux and salt rejection: a vacuum filtration method and a monomer dispersion method. In both cases, various quantities of CNCs and TOCNs were incorporated into a polyamide TFC membrane via in-situ interfacial polymerization. The flux and rejection performance of the resulting membranes was evaluated, and the membranes were characterized via ATR-FTIR, TEM, and AFM. The best improvement was obtained via the monomer dispersion method at 0.5 wt% TOCN loading resulting in a 260% increase in water flux and an increase in salt rejection to  $98.98 \pm 0.41\%$  compared to  $97.53 \pm 0.31\%$  for the plain polyamide membrane. The increased flux is attributed to the formation of nanochannels at the interface between the high aspect ratio nanocrystals and the polyamide matrix. These nanochannels serve as rapid transport pathways through the membrane, and can be used to tune selectivity via control of particle/polymer interactions.

**MONDAY 12:00 pm** - Ballroom 4

**4f - If one were to develop a new NF/RO membrane, specifically for uncharged organic solute rejection, how permeable could it be to water while meeting organic solute rejection goals?**

Eric Hoek (UCLA)\*

Today, we have commercially available NF/RO membranes with separation performance ranging from high-divalent/low-monovalent rejecting NF membranes up to seawater RO membranes exhibiting >99.85% TDS rejection, and everywhere between. However, few NF or RO membranes were specifically developed with the removal of uncharged organic solutes, which may be present at trace levels in drinking water sources and higher levels in wastewater effluents. For over a decade, we have explored the transport of environmentally-relevant uncharged organics (NDMA, 1,4-dioxane, methanol, etc.) through theoretically-modeled, hand-cast, commercially-available NF/RO membranes. We now have a solid practical understanding of the fundamental relationships between membrane structural (or "physical") descriptors such as apparent pore radius and structure factor (which are determined from thin film thickness and free volume along with support membrane pore structure), in addition to the thermodynamic (or "chemical") descriptors such as the solute-membrane partition coefficient (which derives from the free energies of interaction of the solute with water, the solute with the membrane and the membrane with water). Herein, we present new results - both experimental and theoretical - on organic transport through commercial NF/RO membranes in the hopes of answering the question, "If one were to develop a new NF/RO membrane, specifically for uncharged organic solute rejection, how permeable could it be to water while meeting organic solute rejection goals?".

**MONDAY 9:30 am** - Kings Garden 1

**5a - Two-Dimensional Membranes for Gas Separation**

Dan Zhao (National University of Singapore)\*

It is highly desirable to reduce the membrane thickness in order to maximize the throughput and break the trade-off limitation for membrane-based gas separation. Two-dimensional (2D) membranes composed of ultrathin nanosheets have been attracting much attention recently because of their ultrasmall thickness that may offer interesting gas separation performance. In this talk, I will introduce our study on the fabrication of 2D membranes for gas separation. Our candidate materials include graphene oxide (GO) and metal-organic frameworks (MOFs). We have identified some important steps in fabricating and testing 2D membranes. In addition, our 2D MOF membranes exhibit responsive gas separation behaviors under the stimuli of temperature or pressure, paving the way for the rational design of smart membranes for H<sub>2</sub> purification and CO<sub>2</sub> capture.

**MONDAY 10:00 am** - Kings Garden 1

**5b - Restricting Lattice Flexibility in Polycrystalline Metal-Organic Framework Membrane for Efficient Carbon Capture**

Deepu Babu (L'Ecole polytechnique fédérale de Lausanne), Kumar Varoon Agrawal (L'Ecole polytechnique fédérale de Lausanne)\*

Polycrystalline membranes based on metal-organic frameworks (MOFs) are advantageous to their nanoporous counterparts owing to a high degree of structural tunability, relatively fast crystallization kinetics, and higher reproducibility [1]. However, achieving an efficient CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> separation, crucial for the energy-efficient carbon capture, has remained a challenge [2]. ZIF-8 possesses a crystallographically-determined pore aperture of 0.34 nm, ideal for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> separations. However, the lattice flexibility and the gate-opening phenomenon in ZIF-8 is a bottleneck in realizing gas-sieving, critical for the membrane-based postcombustion capture, and selectivities have remained below 5 [3]. In this presentation, I will report a novel post-synthetic treatment, which drastically improves the capture performance of the ZIF-8 films [4]. Lattice stiffening is confirmed by the appearance of a temperature-activated transport, attributed to a stronger interaction of gas molecules with the pore aperture, with activation energy increasing with the molecular size (CH<sub>4</sub> > CO<sub>2</sub> > H<sub>2</sub>). High CO<sub>2</sub>/CH<sub>4</sub>, CO<sub>2</sub>/N<sub>2</sub>, and H<sub>2</sub>/CH<sub>4</sub> selectivities of up to 32.5, 29.3, and 175, respectively, and complete blockage of C<sub>3</sub>H<sub>6</sub> is achieved. Spectroscopic and X-ray diffraction studies confirm that while the coordination environment and crystallinity is unaffected, lattice distortion and strain are incorporated in the ZIF-8 lattice, increasing the lattice stiffness. Overall, this method can improve the separation performance of several MOF membranes. References: [1] N. Rangnekar, N. Mittal, B. Elyassi, J. Caro, M. Tsapatsis, Chem. Soc. Rev. 2015, 44, 7128; [2] H. Yin, J. Wang, Z. Xie, J. Yang, J. Bai, J. Lu, Y. Zhang, D. Yina, J. Y. S. Lin, Chem. Commun. 2014, 50, 3699. 3. C. Zhang, R. P. Lively, K. Zhang, J. R. Johnson, O. Karvan, W. J. Koros, J. Phys. Chem. Lett. 2012, 3, 2130. 4. D. J. Babu, G. He, M. T. Vahdat, P. A. Schouwink, M. Mensi, K. V. Agrawal, Submitted.

**MONDAY 10:30 am** - Kings Garden 1

**5c - New Asymmetric and Permselective Carbon Molecular Sieve Membranes**

Jay (Junqiang) Liu (The Dow Chemical Company)\*, Ted Calverley (The Dow Chemical Company), Dean Millar (The Dow Chemical Company), Mark Brayden (The Dow Chemical Company), Marcos Martinez (The Dow Chemical Company)

Microporous Carbon Molecular Sieve (CMS) membranes have shown excellent intrinsic permselectivities. However, industrially relevant defect-free asymmetric CMS membranes has been a challenge due to the melting and softening of most of the precursors during pyrolysis (decomposition temperature higher than glass transition temperature). In this talk, we will present a novel asymmetric CMS membrane derived from low cost polyvinylidene chloride copolymers (PVDC). PVDC dehydrochlorinate and crosslink before melting, which "locks" the morphology from polymer to carbon. We made for the first time asymmetric PVDC membranes using a phase inversion process and turned them into highly asymmetric Carbon Molecular Sieve (CMS) membranes using a two-step pyrolysis process. The PVDC copolymer composition, solution formulation, and casting conditions were optimized. The asymmetric CMS membranes showed very high permeances of 320 GPU for CO<sub>2</sub> and 8 GPU for C<sub>3</sub>H<sub>6</sub>, while maintaining good selectivities of 21 for CO<sub>2</sub>/CH<sub>4</sub> and 8 for C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub>. The asymmetric CMS membranes were repeatedly synthesized without statistically significant variation. The CMS membranes also have limited change of separation performance during the six months of N<sub>2</sub> storage.

**MONDAY 11:00 am** - Kings Garden 1

**5d - Hitz zeolite membrane separation system (HDS) for gas separation**

Masaya Itakura (Hitachi Zosen Corporation)\*, Satoshi Imasaka (Hitachi Zosen Corporation), Kentaro Shinoya (Hitachi Zosen Corporation), Masashi Okada (Hitachi Zosen Corporation)

Hitachi Zosen Corporation (Hitz) has actively developed and commercialized our zeolite membrane separation systems for several kinds of industry use in liquid- and gas-separation. Hitz membrane elements are 16 mm in diameter and 1130 mm in length. The element is composed of a Al<sub>2</sub>O<sub>3</sub> porous support tube with a closed end and a zeolite thin film deposited on outer surface of the tube by a hydrothermal synthesis process. The element constitution is only inorganic material, which enables the membrane to be used under high temperature and high-pressure conditions. We have developed six varieties of zeolite membranes (HZM-1 to HZM-6) with different composition, pore size and chemical affinity and the optimized zeolite membrane is selected depending on the separation use and the customer requirement. Regarding the gas separation application, for example, in the CO<sub>2</sub> separation performances of HZM-4 membrane for CH<sub>4</sub> upgrading the CO<sub>2</sub> permeance and the selectivity were 1.5 × 10<sup>-6</sup> mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup> and 115 at 313 K, respectively. These permeance and separation performances were much higher than previous reports. Moreover, the permeance and separation performances retained under the coexistence water of 0.35 vol% in CH<sub>4</sub>/CO<sub>2</sub> gas mixture. Hitz zeolite membrane system (HDS) for the CH<sub>4</sub> upgrading produce CH<sub>4</sub> at the yield of 99%. In addition, HZM-2 and HZM-6 membrane also has high potential for purification of hydrocarbons. For example, these membranes exhibit the good performance of olefin/paraffin separation and n/i-paraffin separation driven by the synergy effect of selective adsorption of the feed gas and molecular sieving function.

**MONDAY 11:30 am** - Kings Garden 1

**5e - Insights on the Carbon Molecular Sieve Structure from Stability and Rejuvenation Tendencies**

Samuel Hays (Georgia Institute of Technology)\*, Oishi Sanyal (Georgia Institute of Technology), Nicholas Leon (Georgia Institute of Technology), Chen Zhang (University of Maryland), Pezhman Arab (Georgia Institute of Technology), William Koros (Georgia Institute of Technology)

Carbon molecular sieve (CMS) hollow fiber membranes provide high surface area-to-volume ratios, scalable manufacturability and excellent separation performance for many key gas-pairs, thereby making CMS a frontrunner for next-generation membranes. Physical aging phenomena in CMS cause reduced permeability and increased permselectivity, analogous that seen in glassy polymer membranes. Unlike polymer membranes, however, physical aging in CMS has been thought to be irreversible, due to the lack of a clearly observable glass transition in CMS. This presentation provides a feasible method to restore permeability loss, thereby demonstrating that CMS physical aging can be significantly reversed. Such physical aging and regeneration results also provide new insights into fundamental features of CMS and provide a deeper understanding of the structure and morphology of this complex material. This presentation will address these features and their implications for practical largescale CMS membranes for several gas pairs.

**MONDAY 12:00 pm** - Kings Garden 1

**5f - Fabrication of zeolitic imidazolate framework ZIF-8 membranes by ligand-induced permselectivation in vapor phase**

Xiaoli Ma (University of Wisconsin-Milwaukee)\*, Prashant Kumar (University of Minnesota), Nitish Mittal (University of Minnesota), Alexandra Khlyustova (University of Minnesota), Prodromos Daoutidis (University of Minnesota), Andre Mkhoyan (University of Minnesota), Michael Tsapatsis (Johns Hopkins University)

ZIF-8 membranes have emerged as a promising energy-efficient technology for gas separations, particularly hydrogen purification and propylene/propane separation. High quality ZIF-8 membranes are typically prepared by solution-based methods such as in situ, seeded growth, counter diffusion and microfluidic processing. In addition to cost and environmental disadvantages, the use of solvents in these methods makes it difficult to control the membrane thickness and defects due to the homogeneous nucleation/growth in the bulk solution and the possible re-dissolution of membrane materials. Here, we developed a vapor-phase processing method to address these challenges. Our method is based on the deposition of ZnO in a porous ceramic support using atomic layer deposition technique, followed by ligand vapor treatment to transform the non-selective ZnO deposits to a selective ZIF-8 membrane. All the precursors are introduced from vapor phase without the use of any types of solvents. The ZIF-8 nanocomposite membranes synthesized exhibit superior separation properties including high selectivity of hydrogen over hydrocarbons, and high propylene/propane separation performance maintained at high feed pressure (> 7 atm). These properties can be attributed to the absence of defects and the unique membrane structure that is partly present on the support surface and partly confined in the mesopores of the support.

**MONDAY 9:30 am** - Kings Garden 5

**6a - Polymers with Side Chain Porosity for Ultrapermearable and Plasticization Resistant Materials for Gas Separations**

Sharon Lin (MIT), Francesco Benedetti (University of Bologna), Yuan He (MIT), Chao Liu (University of Chinese Academy of Sciences), Yanchuan Zhao (University of Chinese Academy of Sciences), Hong-Zhou Ye (MIT), Troy Van Voorhis (MIT), Maria Grazia De Angelis (University of Bologna), Timothy Swager (MIT), Zach Smith (MIT)

There are very few solution-processable, linear polymers currently reported that have both ultrahigh CO<sub>2</sub> permeability and high selectivity. All of these structures possess rigid polymer backbones that result in poor polymer chain packing, leading to ultramicroporosity in solid-state chain-entangled films. We report the gas transport properties of two porous polymers obtained via Ring Opening Metathesis Polymerization (ROMP), CF<sub>3</sub>-ROMP and OMe-ROMP, which both possess flexible polymer backbones with rigid side chains. Both OMe-ROMP and its fluorinated counterpart, CF<sub>3</sub>-ROMP, exhibit exceptional plasticization resistance (CO<sub>2</sub> plasticization pressure > 51 bar). CF<sub>3</sub>-ROMP also possesses ultrahigh CO<sub>2</sub> permeability (> 21000 Barrer). In addition, the rate of physical aging for both CF<sub>3</sub>-ROMP and OMe-ROMP is slower than that of traditional polymers of intrinsic microporosity (PIMs), especially for gases with small effective diameters (He, H<sub>2</sub>, and O<sub>2</sub>). The strategy of using ROMP to generate new polymers that have flexible backbones and rigid, pore-forming side chains shows promise for future studies.

**MONDAY 10:00 am** - Kings Garden 5

**6b - Bench scale testing of next generation hollow fiber membrane modules at subambient conditions at the National Carbon Capture Center**

David Hasse (Air Liquide)\*, Shilu Fu (Air Liquide), Sudhir Kulkarni (Air Liquide), Trapti Chaubey (Air Liquide), Alex Augustine (Air Liquide), Andrew Hamilton (Air Liquide), Monaca Mcnall (Air Liquide)

Air Liquide is developing a hybrid CO<sub>2</sub> capture process based on sub-ambient temperature membrane operation in combination with cryogenic distillation (Ref 1-3). Prior work has shown extremely attractive membrane performance. The current work seeks to demonstrate performance of a commercial-scale, high-permeance hollow-fiber membrane, with actual flue gas from a coal fired power plant. Bench scale testing at 1,000 NM<sup>3</sup>/hr scale at the National Carbon Capture Center (NCCC, Wilsonville AL) is being conducted in a field-test unit incorporating pre-treatment, compression, drying, and auto-cooling steps using commercial scale membrane bundles. The membranes can be tested at pressures up to 16 bar with temperatures as low as -65°C. Results from the ongoing long-term testing of the high-permeance PI-2 membrane at NCCC will be presented. An updated techno-economic analysis will be shown along with a discussion of the impact / reduction of impurities (SOX / NOX / metals) in the cold membrane process. In addition, the PI-2 data will be placed in context with additional polymers over an extended temperature range (as low as -65°C) with CO<sub>2</sub>/N<sub>2</sub> selectivity >200. Acknowledgement: Current development work is supported by the Department of Energy, National Energy Technology Laboratory under Award Number DE-FE0026422 (A. O'Palko, J. Figeroa, Program Managers). Prior work presented here was done under Award Number DE-FE0013163. References: 1. CO<sub>2</sub> Capture by Cold Membrane Operation with Actual Power Plant Flue Gas, Final Scientific Report, <https://www.osti.gov/servlets/purl/1373105> 2. 2017 NETL CO<sub>2</sub> Capture Technology Project Review Meeting <https://www.netl.doe.gov/sites/default/files/2017-12/A-Augustine-Air-Liquide-Hollow-Fiber-Modules.pdf> 3. Energy Procedia Volume 63, Pages 186-193 (2014) <http://www.sciencedirect.com/science/article/pii/S1876610214018347>

**MONDAY 10:30 am** - Kings Garden 5

**6c - A Carbon Molecular Sieve Membrane-Based Reactive Separation Process for Pre-Combustion CO<sub>2</sub> Capture**

Mingyuan Cao (University of Southern California), Linghao Zhao (University of Southern California), Dongwan Xu (University of Southern California), Secgin Karagoz (University of California, Los Angeles), Patricia Pichardo (University of California, Los Angeles), Richard J. Ciora, Jr. (Media and Process Technology, Inc.), Paul Kt Liu (Media and Process Technology, Inc.), Vasilios I. Manousiouthakis (University of California, Los Angeles), Theodore T Tsotsis (University of Southern California)\*

Reactive separation processes, such as membrane reactors (MRs) and adsorptive reactors (ARs), are attracting increased interest for industrial applications. We study here a hybrid system combining a MR and an AR in tandem (with the AR following the MR, and the MR's reject stream serving as the AR's feed). We apply this system to the water gas shift reaction (WGS) in the context of its application in the IGCC process for H<sub>2</sub> generation and simultaneous CO<sub>2</sub> capture from coal/biomass. The MR-AR hybrid system under study attains a high WGS reaction conversion exceeding equilibrium, produces a pure H<sub>2</sub> product for power generation, and delivers a high-pressure CO<sub>2</sub> stream ready for sequestration. In our research, specifically, we use carbon molecular sieve (CMS) membranes. Following the field-testing and performance-validation of these CMS membranes under coal/biomass gasification conditions, experiments have been carried-out in the laboratory to determine the membrane characteristics, and the MR performance under the IGCC-relevant conditions, i.e., for temperatures up to 300°C and pressures up to 25 bar, with different syngas compositions. As part of this work, a detailed model for the MR/AR system was also developed and validated using the experimental data. Using this model, a technical and economic analysis (TEA) was carried-out for process design/optimization and economic evaluation of the WGS-MR/AR system for a broad range of operating conditions and design parameters. The experimental and model findings manifest the ability of the WGS-MR/AR process to operate under the desired conditions and to improve the efficiency of the WGS reaction. They demonstrate, in addition, the potential of the system to carry out the in-situ separation of H<sub>2</sub> and CO<sub>2</sub> using the CMS membranes. We conclude from our study, that the CMS-membrane-based WGS-MR/AR system is a good candidate technology for incorporation into IGCC power plants for environmentally-benign power generation.

**MONDAY 11:00 am** - Kings Garden 5

**6d - Synthesis of Polymers of Intrinsic Microporosity (PIM-1) with Poly(ethylene glycol) for Membrane Application**

Volkan Filiz (Helmholtz-Zentrum Geesthacht)\*, Gisela Bengtson (Helmholtz-Zentrum Geesthacht), Silvio Neumann (Helmholtz-Zentrum Geesthacht)

Polymers of intrinsic microporosity have been and continue to be the objects of many research papers since Budd and McKeown launched their first publication about PIM-1 in 2004. PIM-1 is a hydrophobic polymer formed as a molecular ladder; the polymer chains cannot pack tightly because of their contorted molecular structure, provided by spiro fused rings in the polymer chain. Thus, intrinsic nanopores are formed resulting in a large inner surface. Membranes prepared from this polymer show a large fractional free volume and therefore high permeability for many gases, but especially for CO<sub>2</sub> (4000 to 10,000 Barrer) because of an also very high solubility. Until now, the leading polymer of intrinsic microporosity PIM-1 has become quite famous for its high membrane permeability for many gases in gas separation, linked, however, to a rather moderate selectivity. The combination with the hydrophilic and low permeable poly(ethylene glycol) (PEG) and poly(ethylene oxides) (PEO) should on the one hand reduce permeability, while on the other hand enhance selectivity, especially for the polar gas CO<sub>2</sub> by improving the hydrophilicity of the membranes. Four different paths to combine PIM-1 with PEG or poly(ethylene oxide) and poly(propylene oxide) (PPO) were studied: physically blending, quenching of polycondensation, synthesis of multiblock copolymers and synthesis of copolymers with PEO/PPO side chain. Blends and new, chemically linked polymers were successfully formed into free standing dense membranes and measured in single gas permeation of N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub> by time lag method. The aim of this study in polymeric membrane research is the combination of PIM-1, the rigid hydrophobic high flux polymer, with hydrophilic poly(ethylene glycol) (PEGs) of various polymer weights to form stable membranes of improved gas separation properties, especially for CO<sub>2</sub>.

**MONDAY 11:30 am** - Kings Garden 5

**6e - High-permeance polymer-functionalized graphene membranes that surpass the postcombustion carbon capture target**

Guangwei He (L'Ecole polytechnique fédérale de Lausanne), Kumar Varoon Agrawal (L'Ecole polytechnique fédérale de Lausanne)\*

Postcombustion carbon capture using high-performance CO<sub>2</sub>-selective membranes has been identified as one of the most energy-efficient routes for reducing CO<sub>2</sub> emissions [1-3]. However, the capture performance, especially the permeance of the state-of-the-art membranes needs to be significantly increased to further improve the appeal of membranes for postcombustion capture, and importantly, reduce the needed membrane area for separation because the capital cost of the membrane modules scales inversely with the permeance. Currently, with the exception of Polaris second generation membranes from Membrane Technology Research which yields a CO<sub>2</sub> permeance of 2000 GPU, there is no membrane technology that reaches the CO<sub>2</sub> permeance significantly higher than 1000 GPU, while maintaining a separation factor of 20 or above in the humid flue gas conditions. In this presentation, I will report a new class of sub-20-nm-thick organic-inorganic hybrid membranes, which we call as SPONG, comprising of nanoporous single-layer-graphene with a high porosity (up to 18.5%), functionalized with CO<sub>2</sub>-philic polymeric chains [4]. The hybrid membranes yield CO<sub>2</sub> permeance sixfold larger (6290 GPU) than the performance target while separating the CO<sub>2</sub>/N<sub>2</sub> mixture mimicking flue gas streams with a separation factor well within the target. Overall, we report a number of membranes that yield CO<sub>2</sub> permeance up to 11790 GPU and CO<sub>2</sub>/N<sub>2</sub> mixture separation factor up to 57.2. The hybrid membrane is conducive for scale-up because of its facile preparation involving simple coating steps. References [1] Merkel, T. C., Lin, H., Wei, X. & Baker, R. J. *Memb. Sci.* 359, 126-139 (2010); [2] Rao, A. B. & Rubin, E. S. *Environ. Sci. Technol.* 36, 4467-4475 (2002); [3] Bara, J. E., Camper, D. E., Gin, D. L. & Noble, R. D. *Acc. Chem. Res.* 43, 152-159 (2009); [4] He G., Huang S., Villalobos L. F., Zhao J., Mensi M., Oveisi E., Rezaei M., Agrawal K. V., Submitted.

**MONDAY 12:00 pm** - Kings Garden 5

**6f - Fabrication of Thin Film Composite Membranes using Microporous Polymer Blends and Polybenzimidazole Nanoporous Supports for CO<sub>2</sub>/N<sub>2</sub> Separation**

Lingxiang Zhu (U.S. Department of Energy National Energy and Technology Laboratory)\*, Surendar Venna (U.S. Department of Energy National Energy and Technology Laboratory), Ali Sekizkardes (Battelle/U.S. Department of Energy National Energy and Technology Laboratory), Victor A Kusuma (U.S. Department of Energy National Energy and Technology Laboratory), David Hopkinson (U.S. Department of Energy National Energy and Technology Laboratory)

Industrial gas separations usually use large-scale (~10,000 m<sup>2</sup> or more/plant) thin film composite (TFC) membranes that are comprised of a thin (100 nm - 1 μm) selective layer and a thick (> 20 μm) porous support layer. Fabrication and scale-up of the TFC membranes depend on selective layer material with good thin film forming ability and a porous membrane support with optimized pore structure (i.e., small pore size and high porosity) and thus minimal gas transport resistance. In this study, we fabricated TFC membranes based on a cost-effective polymer of intrinsic microporosity/ether side chain polyphosphazene (PIM-1/MEEP) blend that is a high-performance CO<sub>2</sub>-selective membrane material developed in-house recently. PIM-1 and MEEP are soluble and miscible in chloroform, rendering PIM-1/MEEP blend exceptional coatability. To accommodate the thin film coating of PIM-1/MEEP, chloroform-resistant polybenzimidazole (PBI) nanoporous supports were fabricated via a phase-inversion method. These PBI nanoporous supports were characterized by the pore size of < 20 nm, surface porosity of ca. 15%, and CO<sub>2</sub> permeance of 250,000 GPU at 25°C. Defect-free sub-micron PIM-1 based TFC membranes were prepared on the PBI supports via a dip coating technique, and their pure- and mixed-gas CO<sub>2</sub>/N<sub>2</sub> separation properties were systematically investigated. For example, 1-μm-thick PIM-1/MEEP TFC membranes showed pure-gas CO<sub>2</sub> permeance of ca. 800 GPU and CO<sub>2</sub>/N<sub>2</sub> selectivity of 28 at 25°C. Their gas separation performance, membrane stability, and aging behavior in flue gas stream at the National Carbon Capture Center would be presented as well. Due to the great CO<sub>2</sub>/N<sub>2</sub> separation performance, good processability, and the easiness in thin film coating of PIM-1/MEEP as exemplified on the flat-sheet PBI membrane supports, this presentation would also discuss the scale-up of PIM-1/MEEP based composite membranes on PBI hollow fiber membrane supports.

**MONDAY 2:00 pm** - Kings Garden 5

**7a - Field trial of spiral-wound facilitated transport membrane module for CO<sub>2</sub> capture from flue gas**

Yang Han (Ohio State University)\*, Witopo Salim (Ohio State University), Kai Chen (Ohio State University), Dongzhu Wu (Ohio State University), Winston Ho (Ohio State University)

A field trial with 1.4 m<sup>2</sup> spiral-wound (SW) membrane modules fabricated from an amine-containing facilitated transport membrane was conducted with actual flue gas at the National Carbon Capture Center (NCCC) in Wilsonville, AL. Prior to the field test, the membrane modules were systematically evaluated with simulated flue gas to identify the optimal operating conditions. Significant responses to various operating conditions have been noted, particularly with respect to the feed flow rate, feed pressure, operating temperature, and CO<sub>2</sub> concentration. The concentration polarization behavior and feed side pressure drop were significantly affected by the choice of feed flow rate, which retroactively influences the stage cut, or the CO<sub>2</sub> recovery of the module. With the actual flue gas, the membrane modules showed ca. 1450 GPU CO<sub>2</sub> permeance and 185 CO<sub>2</sub>/N<sub>2</sub> selectivity at 67°C with feed and permeate pressures of 4 and 0.3 atm, respectively. The module performance results were essentially identical to those obtained from both membrane modules and flat-sheet membrane samples tested at OSU using simulated flue gas. A 500-h stability was demonstrated despite the interference of system upsets and flue gas outages at NCCC. During the field trial, carbon capture rates of better than 40% were achieved by a single SW module with coal-derived flue gas. Except for a few flue gas upsets, the CO<sub>2</sub> purities in the captured stream were 94.5% or better on dry basis. In addition, a short transient time of the membrane system was observed, which benefits the dynamic integration of the carbon capture technology into the power plant. Further analysis of the tested membrane revealed that no significant amounts of Cr, As and Se were deposited onto the membrane. The data obtained from this project validate the membrane material and provide basis for the design and fabrication of full-scale SW module with a membrane area larger than 50 m<sup>2</sup>.

**MONDAY 2:30 pm** - Kings Garden 5

**7b - Gen-2 Proteus™ membrane and module development for CO<sub>2</sub> capture from gasification streams**

Witopo Salim (Membrane Technology & Research Inc.)\*, Karl Amo ( Membrane Technology & Research Inc.), Trevor Carlisle (Oregon State University), Richard Baker (Membrane Technology & Research Inc.), Jenny He (Membrane Technology & Research Inc.), Jay Kniep (Membrane Technology & Research Inc.), Tim Merkel (Membrane Technology & Research Inc.), Vincent Nguyen (Membrane Technology & Research Inc.), Zhen Sun (Membrane Technology & Research Inc.), Jonathan Tan (Membrane Technology & Research Inc.), Bob Watson (Membrane Technology & Research Inc.), Erik Westling (Membrane Technology & Research Inc.)

Gasification of coal, biomass or other feedstocks is widely used in industry for the production of chemicals and power. In a carbon-constrained world, gas separation is an increasingly important step to maintain the economic viability of these processes with CO<sub>2</sub> capture. Membrane Technology and Research Inc. has previously proposed a dual membrane process for CO<sub>2</sub> capture from gasification processes, including Proteus™ membranes for H<sub>2</sub> removal or purification and Polaris™ membranes for CO<sub>2</sub> recovery. This dual-membrane process can achieve a H<sub>2</sub> recovery of 99% with >90% CO<sub>2</sub> capture while producing high purity liquid CO<sub>2</sub> at an energy cost lower than conventional technology. This presentation focuses on the development of the H<sub>2</sub>-selective Proteus membranes and modules. Field test results of Gen-1 Proteus bench-scale modules with a syngas slipstream at the National Carbon Capture Center (NCCC) in Wilsonville, AL showed promising results over 9,000 hours of testing. Membranes and modules showed H<sub>2</sub>/CO<sub>2</sub> selectivities of 15 or more when treating real syngas containing up to 800 ppm H<sub>2</sub>S. Based on these results, a preliminary techno-economic analysis of the MTR dual-membrane process resulted in a CO<sub>2</sub> capture cost of \$49/tonne of CO<sub>2</sub>, which is approximately 20% lower than the cost for the conventional absorption technology, Selexol™. New Gen-2 Proteus membrane under development at MTR will further reduce costs with an improved upper temperature limit and selectivity compared to Gen-1 Proteus. Initial field test results of the Gen-2 Proteus membrane at NCCC will be presented and future plans of Gen-2 Proteus membrane and module development will be discussed.

**MONDAY 3:00 pm** - Kings Garden 5

**7c - One-pot surface modification of nanocellulose fibrils and effect of manipulated fibril surfaces in Hybrid Facilitated Transport Membranes for CO<sub>2</sub> capture**

Saravanan Janakiram (Norwegian University of Science and Technology)\*, Xinyi Yu (Norwegian University of Science and Technology), Luca Ansaloni (SINTEF Industry), Zhongde Dai (Norwegian University of Science and Technology), Liyuan Deng (Norwegian University of Science and Technology)

The successful use of membranes in CO<sub>2</sub> capture processes is governed by selection of appropriate membrane materials that has preeminent permeation, chemical and mechanical properties. Facilitated transport membranes have been proven to have superior permeation properties under humid conditions. These membranes transport CO<sub>2</sub> through reactional pathway in addition to solution diffusion. The transport properties of these materials can further be enhanced by incorporation of various fillers to result in hybrid membranes. The fabricated hybrid membranes synergistically inherit individual properties of both polymer and filler phase with properties that arise due to their interaction. Nanocellulose fibrils (NFCs) represent a class of renewable 1D bio nanomaterial. Thanks to their high aspect ratio, good mechanical properties, ability to form hydrogen bonding and bio-based origin, NFCs are considered one of the most promising candidate for the processing of polymer nanocomposites. Surface chemistry plays an important role determining the compatibility of nanocellulose fibrils with the polymer matrix. Different surface interactions lead to varying interfaces, which dominate the transport properties of the hybrid matrix. To study the effect of varying interfaces, NFC fibrils have been grafted with different small polymeric moieties using a rapid one-pot functionalization procedure mediated by EDC/NHS. The modified fillers were dispersed in sterically hindered polyallyl amine blend with polyvinyl alcohol and thin film composite membranes with selective layer thickness less than 300 nm were fabricated and tested. NFC functionalized with 4-arm polyethylene glycol resulted in good surface compatibility with matrix polymer leading to a superior gas permeation performance with CO<sub>2</sub> permeance as high as 650 GPU and highest CO<sub>2</sub>/N<sub>2</sub> selectivity of 51 at varying compositions.

**MONDAY 3:30 pm** - Kings Garden 5

**7d - DDR-type zeolite membrane: The first opportunity in CO<sub>2</sub>-EOR industry**

Junya Okazaki (JGC Corporation)\*, Hiroaki Hasegawa (JGC Corporation), Nobuyasu Chikamatsu (JGC Corporation), Kenji Yajima (NGK Insulators), Katsuya Shimizu (NGK Insulators), Makiko Niino (NGK Insulators)

JGC Corporation (JGC) has announced the launch of a joint demonstration test with Japan Oil, Gas and Metals National Corporation (JOGMEC) on CO<sub>2</sub> recovery using a DDR-type zeolite membrane system, which has been co-developed by NGK Insulators, Ltd. (NGK) and JGC, to recover CO<sub>2</sub> from the associated gas of a CO<sub>2</sub>-EOR (Enhanced Oil Recovery) oil field in Texas. To the best of our knowledge, our test is the first pilot scale experience of the use of zeolite membrane for the CO<sub>2</sub>-EOR industry. The membrane has been fabricated by NGK as the world's largest zeolite membrane element to meet the needs of CO<sub>2</sub> separation in natural gas and CO<sub>2</sub>-EOR industries. A thin and defect-free zeolite membrane is prepared onto the inner surface of a cylindrical monolithic porous alumina substrate having 1600 channels with a 180 mm in diameter and 1000 mm in length. Its surface area reaches 12 m<sup>2</sup> which is 200-300 times larger than conventional tubular type zeolite membranes of the same length. Recently, the interest in the practical application of CO<sub>2</sub>-EOR has been growing rapidly. Since CO<sub>2</sub> purchase costs often account for most of the operating expense of a CO<sub>2</sub>-EOR project, CO<sub>2</sub> recovery from associated gas to re-use is essential. For this purpose, polymer membranes are generally applied; however, their insufficient durability often increases the membrane replacement cost. On the other hand, the DDR-type zeolite membrane is not damaged by CO<sub>2</sub> even in very high CO<sub>2</sub> concentration conditions with elevated pressure. Moreover, it shows superior CO<sub>2</sub> permselectivity over hydrocarbons compared to polymer membranes. In this presentation, the advantage of the DDR-type zeolite membrane for CO<sub>2</sub> recovery from CO<sub>2</sub>-EOR associated gas will be discussed. In addition, our recent activity for the demonstration test of the DDR-type zeolite membrane will also be introduced.

**MONDAY 4:00 pm** - Kings Garden 5

**7e - Coating of hollow fiber membrane for carbon molecular sieve membrane preparation**

Yuhe Cao (Georgia Institute of Technology)\*, Kuang Zhang (Georgia Institute of Technology), Oishi Sanyal (Georgia Institute of Technology), William Koros (Georgia Institute of Technology)

This article provides a process for preparing an economical dual-layer asymmetric carbon molecular sieve (CMS) hollow fiber membrane having improved gas separation performance properties. The economically favored process comprises coating engineered support layer fibers to form a dense skin layer in a CMS precursor. Vinyltrimethoxysilane (VTMS) treatment was then employed to the coated precursor fibers, which suppressed the collapse during aggressive pyrolysis processing. Coated precursor fiber membranes were pyrolyzed, and the resultant CMS hollow fiber membranes were investigated for CO<sub>2</sub>/CH<sub>4</sub> separation. CMS permeation results using CO<sub>2</sub>/CH<sub>4</sub> (50:50) mixed gas CMS showed high CO<sub>2</sub>/CH<sub>4</sub> selectivity and high CO<sub>2</sub> permeance.

**MONDAY 4:30 pm** - Kings Garden 5

**7f - Ultraparpermeable benzotriptycene-based PIMs that redefine the upper bounds for CO<sub>2</sub> separations**

Alessio Fuoco (CNR)\*, Bibiana Comesaña-Gándara (University of Edinburgh), Jie Chen (University of Edinburgh), Grazia Bezzu (University of Edinburgh), Mariolino Carta (Swansea University), Ian Rose (University of Edinburgh), Maria-Chiara Ferrari (University of Edinburgh), Johannes Carolus (John) Jansen (CNR), Elisa Esposito (CNR), Marcello Monteleone (CNR), Neil McKeown (University of Edinburgh)

Gas separation by polymeric membranes is an expanding technology for a number of industrial applications such as oxygen or nitrogen separation from air (i.e. separation O<sub>2</sub>/N<sub>2</sub>) or natural gas treatment and biogas upgrading (i.e. separation CO<sub>2</sub>/CH<sub>4</sub>). However, a further enhancement of the polymer transport properties is desirable to be cost effective in comparison with the traditional separation technology currently applied for CO<sub>2</sub> capture or removal. Up to now, only poly(trimethylsilylpropyne) (PTMSP) and few other polyacetylenes demonstrate ultraparpermeability (P>20000 Barrer), but their industrial application is prohibited by their very poor gas selectivity. In this presentation, we report a series of ultraparpermeable PIMs, based on benzotriptycene units, showing substantially higher selectivity than PTMSP [1]. Their extraordinary transport properties are attributable to the inefficient packing of their 2D polymeric chains which results in large interconnected pores that enhance gas permeability. We will show that the outstanding CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> permselectivity of the whole family of benzotriptycene PIMs allows the introduction of a new upper bound to define the current state-of-the-art. The gas transport properties will be discussed in terms of permeability, diffusivity and solubility. For selected samples, a novel instrument will be used to determine not only mixed gas permeability, but also the diffusion coefficient of gas mixtures [2]. Ageing data and the effect of the temperature on the transport properties will be also discussed. Finally, we will anticipate the potential exploitation of these materials for large scale gas separation application. References [1] I. Rose et al., Polymer ultraparpermeability from the inefficient packing of 2D chains, Nat. Mater. 16 2017. [2] S.C. Fraga et al., A Novel Time Lag Method for the Analysis of Mixed Gas Diffusion in Polymeric Membranes by On-Line Mass Spectrometry: Method Development and Validation. J. Memb. Sci. 561 2018.

**MONDAY 2:00 pm** - Ballroom 3

**8a - CFD simulation of crimped hollow fiber membranes for liquid separation processes**

Mohammad Younas (University of Engineering and Technology, Peshawar), Amir Muhammad (University of Engineering and Technology, Peshawar), Glenn Lipscomb (University of Toledo)\*

Hollow fiber membrane contactors are considered a promising technology for intensification of separation processes ranging from haemodialysis to dehydration. Module performance depends on membrane materials, transport properties and module design parameters that control fluid flow through the module and the resulting development of permeation limiting boundary layers. If fluid boundary layer resistances are significant, module designs that introduce a cross-flow component to the shell flow can be beneficial. This can be done through the use of baffles and/or knitted fibers. Alternatively, crimped fibers can be used to introduce a cross-flow velocity component [1, 2]. Computational fluid dynamics (CFD) is used widely to simulate fluid flow in various areas of research. Commercial codes include COMSOL Multiphysics and Ansys Fluent which use the Finite Element Method (FEM) and Finite Volume Method (FVM) for discretization of the governing conservation equations, respectively. Commercially available HFMC module was taken for modelling and simulation of liquid-liquid extraction in this work. Simulations were performed for a flow-cell containing a single fiber based on symmetry considerations. The simulation domain was limited further to a short repeating segment of the fiber in the cell. The repeat unit of the flow-cell was created by translating the center of a circle along a sine wave with varying values of fiber diameter, crimp amplitude and crimp wavelength. Numerical approximations to the equations were obtained using COMSOL Multiphysics and Ansys. The geometry and mesh were created within each software and the same geometrical parameters for the flow-cell and boundary conditions were used. The model was validated with prior experimental results [3]. Velocity and concentration profiles were evaluated throughout the flow-cell. The study revealed that CFD is a promising tool for the simulation of coupled hydrodynamics and mass transfer processes.

**MONDAY 2:30 pm** - Ballroom 3

**8b - Computational Fluid Dynamics Modeling for the Investigation of Multi-Layer Spacer Effects**

Zachary Binger (The University of Arizona), Andrea Achilli (The University of Arizona)\*

Forward osmosis (FO) and pressure retarded osmosis (PRO) are processes of interest for applications in water purification and energy recovery. By reducing hydrodynamic losses within membranes and maximizing the experienced osmotic pressure difference between streams, FO and PRO can be used to recover potable water from wastewater more efficiently and/or reduce the cost of desalination. The development of computational fluid dynamics (CFD) models, can be used to investigate the effectiveness of spacer geometries in reducing pressure loss and increasing water flux in FO and PRO. CFD work easily interfaces with 3D printing to create rapid prototyping to support experimental work. The geometries created with computer-aided design software for CFD simulation can be used by additive manufacturing machines such as 3D printers to get rapid prototyping for the physical testing of any CFD experiment. 3D printing techniques have the ability of printing resolutions down to 25 microns resulting in high resolution and smooth surfaces. This allows for creation of spacer shapes that would not be possible with traditional manufacturing techniques in addition to instant results for improving ensuing spacer designs. This research focuses on the use of multi-layer spacers to promote vortex shedding and improve water flux by reducing or eliminating stagnant eddies that form along membrane walls. CFD models have been created at the bench scale, approximately 100 cm<sup>2</sup>, to investigate the effectiveness of multi-layer spacer geometries on vortex shedding. Implementing smaller wing-shaped filaments between larger mid-channel spacers can promote vortex shedding while still achieving redirection of low concentration bulk towards membrane walls. The wing-shape spacer will magnify horizontal velocities directed toward regions that stagnant eddies occupy, effectively breaking them up and increasing water flux while minimizing the increased pressure losses that the larger number of spacers cause.

**MONDAY 3:00 pm** - Ballroom 3

**8c - Direct numerical simulation of unsteady mixing in direct contact membrane distillation systems with membrane spacers**

Jincheng Lou (Colorado School of Mines)\*, Jacob Johnston (Colorado School of Mines), Nils Tilton (Colorado School of Mines)

Direct contact membrane distillation (DCMD) is a thermal process in which warm feed and cool distilled water flow on opposite sides of a hydrophobic membrane. The temperature difference causes water to evaporate from the feed, travel through the membrane, and condense in the distillate. To date, CFD studies of DCMD focus primarily on the challenge of temperature polarization. For high concentration brines, however, concentration polarization is another major challenge that reduces system efficiency and leads to mineral scaling. In addition, unsteady mixing triggered by flow over membrane spacers is also not well understood. To study coupled temperature polarization, concentration polarization, and unsteady mixing in the DCMD treatment of high concentration brines, we develop an in-house CFD method for simulating 2-D heat and mass transport in plate-and-frame DCMD systems with cylindrical spacers. The coupled momentum, energy, and mass transport equations are solved using a finite-volume method with an efficient non-iterative unsteady scheme. The membrane spacers are simulated using recent advances in immersed boundary methods. We investigate temperature and concentration polarization under various operating conditions and spacer placement. At low Reynolds numbers, we find the flow is steady, with recirculation zones behind the spacers. At high Reynolds numbers, we find that the flow transitions to an unsteady regime with vortex shedding. For both regimes, the recirculation zones and vortices interact with the membrane surfaces, forming regions of high and low polarization, with corresponding variations in transmembrane heat and vapor flux.

**MONDAY 3:30 pm** - Ballroom 3

**8d - Concentration polarization modeling for high-pressure membranes with engineered surface features**

Zuo Zhou (Clemson University)\*, David Ladner (Clemson University), Sapna Sarupria (Clemson University), Steven Weinman (Clemson University), Scott Husson (Clemson University), Ilenia Battiato (Stanford University), Negin Kananizadeh (Clemson University)

The goal of this research is to develop a computational framework to predict concentration polarization (CP) of patterned membranes designed for purification of saline or impaired waters. Extensive literature has studied the use of surface coatings on membranes to reduce fouling. More recently it has been proposed that the surface morphology can be modified (surface patterning) to give membranes fouling resistance, similar to what is seen in nature (i.e., shark skin). CP, a mass transfer related phenomenon, is an important driver for fouling. Our research hypothesis is that certain pattern geometries can significantly reduce membrane fouling by reducing CP. The work presented here focuses on computational fluid dynamics (CFD) modeling to simulate different surface features and evaluate how fluid flows in the space above the membrane. The computational models were built to simulate membranes patterned in the lab with a silicon stamp. The stamp produced a variety of surface features including line and grooves, pillars, and pyramids. The surface features varied in size from 2  $\mu\text{m}$  to 512  $\mu\text{m}$  with a pattern depth of 1  $\mu\text{m}$  to 256  $\mu\text{m}$ . Simulations evaluated the effects of velocity, concentration distribution, and shear stress on the fluid flow around the features. Velocity profiles showed that the surface features alter the fluid path, resulting in a lower velocity in between features, but a faster velocity on the elevated regions. Lower shear stress was observed in the valley region of the patterns, corresponding to higher concentration results. In general, patterns always increase CP, and this is due to the increased boundary layer thickness caused by higher roughness. Mass transfer coefficient was the highest among flat membranes. Analytical solutions were used to compare with the numerical results among flat membranes, confirming that the models predicted the results very well.

**MONDAY 4:00 pm** - Ballroom 3

**8e - Analysis of Micromixers to Minimize Scaling Effects on Reverse Osmosis Membranes**

Jeremy Walker (U.S. Army)\*, Shawn McElmurry (Wayne State University), James Dusenbury (U.S. Army)

The standard diamond-shaped mesh spacers commonly used in spiral wound membrane elements results in non-ideal hydrodynamics that can lead to fouling, which ultimately reduces the flux of water through the membrane and the operational life of the unit. To address this shortcoming, a novel method for separating RO membrane leaves in spiral wound elements was developed and evaluated. Three-dimensional (3-D) printing was utilized to manufacture micromixers directly on membrane swatches. To enhance performance, a two-dimensional computational fluid dynamic model was used to select the optimal geometry and pattern of 3-D printed micromixers. The optimal geometry selected created unhindered flow between 0.2 m/s and 0.3 m/s, using an inlet flow velocity of 0.104 m/s, across 40% of the membrane surface. Laboratory experiments were conducted to evaluate the performance of micromixers and compared to unmodified membranes with a standard 20 mil (0.508 mm) mesh feed spacer. Pure water flux and salt rejection were found to be similar to standard membranes, indicating the 3-D printing process did not damage intrinsic membrane properties. Calcium sulfate scaling experiments were conducted. Scale initially began to form within 2 hours of treatment resulting in a flux decline of approximately 10% for both modified and unmodified membranes. Over 14 hours, an average flux decrease of 24% was observed for modified membranes compared to an average flux decrease of 78% for the unmodified membranes. This demonstrated the improved resistance to fouling created by the open channel design with optimal flow conditions. Micromixers printed directly to the membrane surface offers the ability to optimize feed channel hydrodynamics, reduce scale formation and minimize flux decline representing a significant advancement in membrane technology.

**MONDAY 4:30 pm** - Ballroom 3

**8f - Do Hydrodynamic Instabilities Cause Roughness in Thin Polyamide Films of Reverse Osmosis Membranes?**

Akshay Deshmukh (Yale University)\*, Puskar Mondal (Yale University), Subhajyoti Chaudhuri (Yale University), Menachem Elimelech (Yale University)

Polyamide films form the all-important selective layer of thin-film composite (TFC) membranes, currently the gold-standard for reverse osmosis (RO) desalination. The physical structure of these thin films plays a critical role in determining key membrane properties, including permeability and selectivity. Recently, several spectroscopic studies have sought to elucidate the structure of polyamide films, which are formed by interfacial polymerization. However, fundamental aspects of polyamide film formation, including the origins of the chaotic ridge and valley morphology, remain unknown. In this study, we examine the potential for hydrodynamic instabilities to cause the extraordinary ridge and valley structure exhibited by thin polyamide films by destabilizing the reaction interface during polymerization. We begin by developing a transient moving-boundary reaction model to determine the rate of reaction between the diamine and tri-acid chloride monomers. We then determine the transient temperature profiles in the aqueous and organic layers as a function of their thermal properties. Finally, these temperature profiles are incorporated into a linear stability analysis that accounts for buoyancy (Rayleigh) and surface tension (Marangoni) forces. The two-layer Rayleigh-Bénard-Marangoni problem is solved using novel semi-analytical methods to account for transient temperature coupling. Our analysis demonstrates the rapid destabilization of the reaction interface by Marangoni forces emphasizing the need to account for surface tension gradients when investigating polyamide film formation. We show that buoyancy forces coupled with surface tension forces can readily lead to instabilities in both the aqueous and organic layers. While further experimental work is required to determine key parameters, including the enthalpy of reaction, our analysis provides a robust platform for assessing the impact of hydrodynamic instabilities on the roughness of thin polyamide films.

**MONDAY 2:00 pm** - Ballroom 4

**9a - Structural and Transport Properties of Membranes in High-Salinity Desalination using Cascading Osmotically Mediated Reverse Osmosis**

Xi Chen (Columbia University)\*, Chanhee Boo (Columbia University), Ngai Yin Yip (Columbia University)

Management and treatment of high-salinity brines ( $>70,000$  ppm TDS) have rapidly risen to be global environmental challenges. We recently proposed a novel cascading osmotically mediated reverse osmosis (COMRO) membrane technology for energy-efficient desalination of hypersaline brines. COMRO utilizes the innovative design of bilateral countercurrent reverse osmosis stages to lessen the transmembrane osmotic pressure difference, thus depressing the hydraulic pressure needed. In COMRO operation, membranes are challenged by the atypical working environments, including high pressures and high salinities. In this study, we experimentally investigate impacts of hydraulic pressures and salinities on structural and transport properties of thin-film composite polyamide membranes in high-salinity desalination using COMRO. Our study shows that raising the hydraulic pressure detrimentally affects the membrane water permeability,  $A$ . After the membrane is completely compacted,  $A$  remains constant under different pressures, and will gradually recover when the membrane is relaxed from pressurization. Our study also indicates that these changes in water permeability are governed by morphological changes in the active-support interlayer of the membrane. Membrane salt permeability,  $B$ , presents similar tendencies to  $A$  as hydraulic pressure changes. The membrane structural parameter,  $S$ , is demonstrated to be consistent at different salinities (0-293,000 ppm TDS). We found that salinities of up to 117,000 ppm TDS does not exhibit significant influence on membrane water permeability, whereas the salt permeability is substantially elevated when the salinity increases (up to 228,000 ppm TDS). This research systematically studies fundamental structural and transport properties of membrane under the high pressure and salinities in COMRO operations to advance the technology, and also provides insights into principal membrane transport mechanisms applicable for all Osmotically-Driven processes.

**MONDAY 2:30 pm** - Ballroom 4

**9b - Utilization of reverse solute diffusion to enhance membrane performance during Osmotically-Driven processes - improved boron retention and silica scaling mitigation**

Yining Wang (Nanyang Technological University)\*, Weiyi Li (Southern University of Science and Technology), Chuyang Tang (University of New South Wales), Rong Wang (Nanyang Technological University)

This study presents the positive effects of reverse solute diffusion (RSD) during Osmotically-Driven processes. In one case, we utilize the reverse solute diffusion (RSD) of ions from alkaline draw solutions (DSs) and the concentration polarization of the hydroxyl ions to create a highly alkaline environment near the membrane active surface. The results show that boron (in feed) rejection can be enhanced by 40% by increasing the pH of NaCl DS to 12.5 in the active-layer-facing-feed-solution (AL-FS) orientation. The effect of RSD enhanced boron rejection was further promoted in the active-layer-facing-draw-solution (AL-DS) orientation, evidenced by the significantly increased boron rejection (from 40% to 90%) with a DS of pH 12. This observation can be explained by the enhanced RSD of  $\text{OH}^-$  as compared with the AL-FS orientation and the presence of concentrative internal concentration polarization (ICP) in the AL-DS, which further increase the local pH at the membrane active surface. Similarly, in another case, silica scaling can be effectively controlled by lowering the pH of the DS in the AL-DS orientation, which can be attributed to the low local pH in the membrane support layer as a result of the ICP of the reversely diffused  $\text{H}^+$ . The current study opens a new dimension for enhancing Osmotically-Driven membrane performance by using tailored DS chemistry, where the RSD-induced localized water chemistry change is taken advantage in contrast to the conventional method of chemical dosing to the bulk feed water.

**MONDAY 3:00 pm** - Ballroom 4

**9c - Osmotic Membrane Desalination Performance Governed by Molecular Reflection at the Liquid-Vapor Interface**

Akshay Deshmukh (Yale University), Jongho Lee (University of British Columbia)\*

Hydrophobic nanoporous membranes that employ osmotically-driven vapor-phase water transport have great potential to simultaneously achieve high rejection of solutes and a high water permeability. While the permeability can be increased by reducing the membrane thickness, recent studies reported that considerable water transport resistances exist at the liquid-vapor interface associated with liquid-vapor phase change, which may limit the permeability enhancement. We develop a new theoretical framework to analyze osmotically-driven water transport across porous hydrophobic membranes by accounting for the transport resistances associated with both diffusion through the membrane and phase-changes at the liquid-vapor interfaces. We systematically derive the functional dependence of the membrane transport resistance on membrane pore size, pore aspect ratio, temperature, and condensation coefficient. A thermodynamic criterion is also derived for minimum membrane thicknesses above which membrane wetting becomes energetically unfavorable. The application of the developed framework to osmotic distillation (OD) reveals that for thick membranes ( $>> 1 \mu\text{m}$ ) water flux is governed by a combination of molecular and Knudsen diffusion, showing an inverse proportionality to the membrane thickness. However, the resistance associated with phase-changes, arising from molecular reflection at liquid-vapor interfaces, becomes the transport-limiting factor as membrane thickness decreases ( $< \sim 1 \mu\text{m}$ ). The framework presented provides key design principles for membrane that utilize vapor transport for a range of applications, including desalination, water treatment, chemical concentration, and energy conversion.

**MONDAY 3:30 pm** - Ballroom 4

**9d - Characterization of External and Internal Fouling of Forward Osmosis (FO) Process Through Ultrasonic Time Domain Reflectometry (UTDR) Method**

Li Lai (Nanyang Technological University)\*, Tzyy Haur Chong (Singapore Membrane Technology Centre)

Forward osmosis (FO) process is playing an increasingly important role in the desalination and wastewater treatment. Recent studies proposed that FO actually has higher fouling propensity, which is masked by self-mitigation effects when water flux decline. Moreover, water flux alone is insufficient to be a sensitive fouling indicator since it can be influenced by several factors apart from fouling. In this regard, the ultrasonic time domain reflectometry (UTDR) method was for the first time applied in fouling detection of FO in real-time manner. The signals are compared, transformed and analysed quantitatively. There are main conclusions: 1. The fluctuation of ultrasonic signal under foulants-free and hydraulic pressure-free channel were tested as 0.15% and 2.10% in 10 mins with respect to the arrival time and amplitude, respectively, and the values served as the threshold of reliable fouling indicators. 2. The amplitude and arrival time shift of selected peaks were adopted to differentiate the formation of cake layer and pore-clogging process, respectively. The amplitude of the first main peak was increased by  $59.82 \pm 8.78\%$  and by  $0.72 \pm 6.05\%$  at the conclusion of fouling process that lasted for 2 hrs on AL-DS mode and AL-FS mode, respectively. The trend of arrival time of the peak is also opposite in different membrane orientations. 3. On AL-FS mode, the cake layer formed on CTA membrane calculated through UTDR was  $32.0 \pm 4.5 \mu\text{m}$ , which was in agreement with the thickness of  $27.4 \pm 0.5 \mu\text{m}$  obtained via mass balance at end of fouling process. On AL-DS mode, the delay of amplitude enhancement on peak amplitude revealed a transition process of silica from fluid to glassy state when colloidal destabilization was prompted by severe ICP due to pore-clogging process. 4. Compared to CTA membrane, less symmetric and more porous TFC membrane imposed challenges on quantitative analysis of ultrasonic signal due to scattering and attenuation effect.

**MONDAY 4:00 pm** - Ballroom 4

**9e - Incorporating membrane deformation into the boundary layer equation to model water and reverse salt flux in osmotic processes**

Jaime A Idarraga-Mora (Clemson University)\*, Alton O'Neal (Clemson University), Morgan Pfeiler (Clemson University), David Ladner (Clemson University), Scott Husson (Clemson University)

Osmotic processes (OP) involve the contact of two solutions with different solute concentration across a membrane interface to generate a water flux. OP utilize spacers with large openings to reduce detrimental concentration polarization. When hydrostatic pressure (HP) is applied in OP, such as in pressure-retarded osmosis (PRO), membranes undergo a mechanical deformation as they are compressed against the spacer. This deformation causes an increased reverse salt flux (RSF) as the HP increases. We developed a model that incorporates membrane deformation into boundary layer equations to describe water and RSF in OP. We deformed three commercial thin-film composite membranes using an Instron machine in creep test mode with the goal of correlating linear membrane strain with transport properties obtained via direct-flow permeation. We performed cross-flow PRO flux measurements and used literature data to train the model for predicting changes in RSF with increased HP. Using laser microscopy we were able to pinpoint the area on the membrane with increased deformation, and to measure the deformation profile. Finally, we correlated our PRO data with the opening size of feed spacer used in each experiment. Results showed that membrane deformation increases with feed spacer opening size at constant HP. The linear membrane strain reaches values above 15%, which are greater than the reported strain-to-fracture values for these membranes. RSF was not statistically different when measured using increasing and decreasing HP profiles, suggesting that membrane deformation is partially reversible. Best fits were obtained using a model that incorporated diffusion through an intact polymer, deformed polymer, and fracture sites. These results indicate that deformations in more than 2% of the membrane area lead to exponential increments in the RSF as HP increases. This work introduces membrane deformation in the design equations of membranes and modules for osmotic processes.

**MONDAY 4:30 pm** - Ballroom 4

**9f - A Thin-Film Forward-Osmosis Membrane Made from a Graphene Oxide-Silver Metal-Organic Framework Nanocomposite: Antifouling and Antibiofouling Assessment**

Mostafa Dadashi Firouzjaei (University of Alabama), Ahmad Arabi Shamsabadi (Drexel University), Mohammad Sharifian Gh (University of Virginia), Milad Rabbani Esfahani (University of Alabama)\*, Ahmad Rahimpour (Babol Noshirvani University of Technology), Masoud Soroush (Drexel University)

Fouling and biofouling are still issues in thin-film nanocomposite (TFN) membranes. This paper describes a TFN membrane fabricated from a novel nanocomposite based on graphene oxide (GO) and a silver metal-organic framework (Ag-MOF). The TFN membrane has a more negative surface charge, higher hydrophilicity, and higher water permeability compared with its thin film composite (TFC) counterpart. Fluorescence imaging revealed that the GO-Ag-MOF TFN membrane kills *E. coli* more than the Ag-MOF TFN, GO TFN, and pristine TFC membranes by 16, 30, and 92%, respectively. Forward osmosis experiments with *E. coli* and sodium alginate solutions showed that the GO-Ag-MOF TFN membrane by far has the lowest water flux reduction among the four membranes, proving the exceptional anti-biofouling and antifouling properties of the GO-Ag-MOF TFN membrane.

**MONDAY 2:00 pm** - Kings Garden 4

**10a - Tannic acid-iron network based green technique for enhanced membrane performance in water reuse**

Hao Guo (The University of Hong Kong)\*

Membrane-based water reuse technologies has arisen as a promising solution to address water scarcity. Currently, reverse osmosis (RO) and nanofiltration (NF) membranes are often used to remove solutes including dissolved ions from water for potential reuse. However, RO and NF are still not adequate enough to retain some organic micropollutants such as endocrine disrupting compounds (EDCs) (e.g., rejection rate as low as 50%), which is significantly jeopardizing the safety and quality associated with water reuse. We first reported a rapid and green techniques using tannic acid (TA)-iron (Fe) coordination networks to improve membrane rejection of organic micropollutants. Various molar ratios of TA-Fe were investigated to form a coating layer on a polyamide-based NF270 membrane. The coating process could be completed within 2 minutes as confirmed by quartz crystal microbalance. XPS analysis indicated the successful coating of TA-Fe on the membrane surface. The coated membrane with TA-Fe molar ratio of 1:3 (i.e., NF270-Fe3) showed the greatest enhanced rejection of NaCl. The rejection of neutral and hydrophilic molecular probes was used to evaluate membrane pore size change. The results showed that NF270-Fe3 had a reduced average pore radius of 0.40 nm compared to that of NF270 membrane (0.44 nm), suggesting the enhanced effect of size exclusion. The TA-Fe coating significantly improved membrane rejection of EDCs and antibiotics, while the highest rejection was achieved by NF270-Fe3. Compared to base NF270 membrane, NF270-Fe3 gave 2-3 times enhancement of rejection for EDCs (i.e., 4-5 times reduction for EDCs permeability) and one order of magnitude reduction of antibiotics permeability. Such a rapid and effective coating technique using green polyphenol-metal network assembly enable TA-Fe being a promising material for large-scale applications.

**MONDAY 2:30 pm** - Kings Garden 4

**10b - Membrane Distillation (MD) and Reverse Osmosis (RO) processes for water recovery from pre-treated high strength brewery wastewater**

Nawrin Anwar (Concordia University)\*, Mahbuboor Choudhury (Concordia University), Saifur Rahaman (Concordia University)

Water recovery and reuse in the industrial sectors through advanced wastewater treatment can be effective means to address the water shortage issue as well as to reduce the wastewater load to the environment. Membrane-based separation processes can be efficient technology for producing freshwater for reuse within the industry thus combating the major challenge of freshwater scarcity. Beer production at brewery industries results in the discharge of a high quantity of wastewater (~3 to 10 L wastewater for 1 L of beer production) containing sugars, ethanol, soluble starch, total suspended solids, and volatile fatty acids. This study aims at investigating the potential of membrane-based separation processes (MD and RO distinctly) for pre-treated brewery wastewater for water recovery and possible reuse. Pre-treated brewery wastewater effluent with a reduction of the substantial amount of organics and total suspended solids was directed to MD and RO separately for enhanced water qualities for possible reuse within the brewery industry. The commercial membranes, implemented in industrial wastewater treatment, were used to evaluate the water recovery in MD, and RO processes through assessing the permeate flux decline, and contaminant rejections. The fouling characterization was observed by the surface morphology, and chemical composition of the membrane surfaces before and after the water recovery operation. Results revealed that both the processes could achieve high removal of organics (>94% COD removal), and nutrients (>99% TN and ~100% TP removal). Lower water flux drop, and higher water recovery were obtained by MD process compared to the RO process for 80 hours operation indicating the potential application of MD as an advanced treatment step for water recovery in food industries with high organic loadings.

**MONDAY 3:00 pm** - Kings Garden 4

**10c - Field Demonstration of Real-Time Colloidal Particle Monitoring to Improve MF and UF Membrane Performance**

Jana Safarik (Orange County Water District)\*, Ganesh Rajagopalan (Kennedy/Jenks Consultants), Helia Safaee (Kennedy/Jenks Consultants), Megan Plumlee (Orange County Water District), Zita Yu (West Basin Municipal Water District)

Low-pressure membrane filtration processes provide reliable water quality for water reuse but are susceptible to fouling. Membrane fouling is attributed to deposition of colloidal particles (<200 nm) inside the membrane pores. Currently, no online techniques are available to directly measure colloidal particles in the feed water, which would facilitate appropriate pretreatment and real-time control. In this study, a real-time monitoring technology was implemented to track colloidal particles concentration and size distribution in the feed water to facilitate their targeted removal via coagulation. The mitigation strategy used Nanoparticles Tracking Analysis (NTA) (NanoSight NS500 by Malvern Instruments) and was tested at two sites: Orange County Water District (OCWD) and West Basin Municipal Water District (WBMWD). The fouling potential for the OCWD microfiltration (MF) pilot receiving targeted polyaluminum (PACl) coagulation was mitigated, with TMP values reduced by 60% after six-weeks compared to the control (no coagulant). Economic evaluation for OCWD's full scale advanced purification plant (100-MGD) indicated that the proposed approach can reduce energy consumption due to microfiltration by 28-35%, resulting in 3 GWh/year of projected energy savings, as well as \$519,700/year of potential savings in membrane cleaning, replacement and operating costs. The ultrafiltration (UF) pilot demonstration at WBMWD targeted PACl coagulation slowed the rate of TMP increase by 43% compared to control and achieved a 63% reduction in energy consumption during pilot operation. This could translate to over 600 MWh/year of energy savings for a 14.4-MGD UF facility as well as potential savings of over \$110,000/year in overall operating and maintenance costs. However, coagulant choice plays a critical role in the success of the targeted pretreatment strategy, as targeted FeCl<sub>3</sub> dosing was not equally successful.

**MONDAY 3:30 pm** - Kings Garden 4

**10d - Selective removal of phosphorus from wastewater using electromembrane process**

Sanhita Chaudhury (Ben-Gurion University of the Negev)\*, Oded Nir (Ben-Gurion University of the Negev)

With increasing demand for wastewater recycling, stricter regulations for phosphorus (P) concentration in the wastewater effluents are being placed, to ensure sustainable discharge and reuse. This requires removing P from effluent as a polishing step, which is mostly done by chemical precipitation, adsorption or membrane technology. However, precipitation and adsorption processes generate high amounts of waste and require substantial amount of chemicals to regenerate sorbent. In membrane-based processes, selectivity for P is low and liquid waste production can be substantial. However, electromembrane-based processes synergistically integrates both adsorption and membrane separation in a manner that can overcome the inherent disadvantages of both methods. With this in view, the present work aims to develop and test membrane-sorption processes for highly selective and efficient removal of P from effluents having low P concentrations. For this purpose, iron oxyhydroxides (hence refereed as FeO) nanoparticles modified membranes were prepared using a two-compartment permeation method, in which FeO nanoparticles were grown in the pores of commercially available polycarbonate track-etched membrane (0.2  $\mu\text{m}$  dia). SEM and XRD methods confirmed the presence of amorphous FeO nanoparticles within the pores of the composite membrane (FeOm). The SEM also indicated that the cylindrical pores of the membrane were completely filled by the FeO nanoparticles (~50-60 nm), which was reflected in the extreme reduction in the water flux through the FeOm as compared to the corresponding pristine membrane. Due to the amorphous structure and nanoscale size of the FeO particles, high P uptake capacity (0.5 mmol/g) and large distribution coefficient ( $\log K_d = 5.5$ ) was obtained. These promising results open interesting routes for chemical free electro-assisted regeneration of the sorbent and for electrodriven selective transport of phosphorus based anionic species.

**MONDAY 4:00 pm** - Kings Garden 4

**10e - Water Recovery from Produced Water via Robust Membrane Distillation**

Rong Wang (Nanyang Technological University)\*

With many production activities, a substantial volume of produced water is generated annually in the oil and gas industry, making it one of the most water-intensive industries. Managing produced water has become a consequential part of the sustainable development of the oil and gas industry due to stringent environmental legislations, severe strain on water resources, and escalating costs of wastewater disposal. Direct-contact membrane distillation (DCMD) holds potential for the recovery of high quality water from produced water. However, membrane fouling and pore wetting are challenging issues for long-term DCMD operations due to the presence of low surface tension species in these waters. Thus, developing robust membranes with anti-fouling and anti-wetting properties for effective produced water treatment is very important. In this presentation, we report our efforts in making novel composite hollow fiber membranes based on co-deposition of polydopamine (PDA)/polyethylenimine (PEI) onto the outer surface of a commercial hydrophobic polyvinylidene fluoride (PVDF) substrate. The successful co-deposition was verified using different characterization techniques. The composite membrane is in-air hydrophilic and underwater superoleophobic that can prevent organics adhesion. The performance of the membrane was investigated via DCMD experiments by feeding a series of low surface tension solutions. The results suggest that the newly developed composite PVDF membrane could potentially be used for long-term water recovery from produced water via DCMD.

**MONDAY 4:30 pm** - Kings Garden 4

**10f - Potable-quality water recovery from primary effluent through an integrated algal-osmosis membrane system**

Lu Lin (New Mexico State University)\*, Wenbin Jiang (New Mexico State University), Pei Xu (New Mexico State University)

A dual algal-osmosis membrane treatment system was studied for the recovery of potable-quality water from primary effluent of a municipal wastewater treatment plant. The core components of the integrated system include a mixotrophic algal process for removal of biochemical oxygen demand (BOD) and nutrients from the primary effluent, followed by a hybrid forward osmosis (FO)-reverse osmosis (RO) system for separation of biomass from the algal effluent and production of potable-quality water. In contrast to traditional wastewater treatment systems, mixotrophic metabolism of the algal system removes BOD and nutrients from the primary effluent through a single-step treatment and eliminates the input of aeration energy and supplemental carbon for denitrification. The hybrid FO-RO system was operated in batch mode and reached water productivity of 1.57 L/m<sup>2</sup>-h in FO using seawater as draw solution; 3.50 L/m<sup>2</sup>-h in brackish water RO (BWRO) and 2.07 L/m<sup>2</sup>-h in seawater RO (SWRO) at 300 psi. Overall, the integrated algal-osmosis membrane system achieved complete removal of ammonia, fluoride, and phosphate; over 90% removal for calcium, sulfate, and organic carbon; 86-89% removal for potassium and magnesium. High resolution mass spectrometry and fluorescence excitation-emission matrix (FEEM) spectrophotometry were used to study the transport and fate of the organic contaminants in the algal and membrane processes. Broadband characterization using the high resolution mass spectrometry revealed broad removal of organic compounds, particularly wastewater surfactants upon algal treatment. Product water generated by the integrated system met both primary and secondary drinking water standards. Cleaning by NaOH solution was found to be effective in removing organic- and bio-fouling of the FO membrane and restoring membrane performance during longer-term algal wastewater filtration (700 hours) and at a water recovery of 90%.

**MONDAY 2:00 pm** - Kings Garden 1

**11a - Ion Transport Through Perforated Nanoporous Graphene**

Mandakranta Ghosh (University of Twente)\*, Koen F. A. Jorissen (University of Twente), Jeffery A. Wood (University of Twente), Rob G. H. Lammertink (University of Twente)

In this work, we investigate the ion transport through a monolayer perforated graphene membrane. We use ion-beam bombardment to create nano pores in graphene supported on a polymer foil in order to study ion-transport across a single-atom thick charge-selective interface (Madauß et al., 2017). The ion selectivity of these 2D membranes are studied with respect to both monovalent and multivalent salts, by measuring the induced potential between two different concentration electrolyte compartments separated by the nanoporous graphene. Our experimental findings remarkably showed that the total electrical potential across a single-layer graphene membrane can be described as a cation-selective layer using a modified version of the Teorell-Meyer-Sievers (TMS) relationship (Ghosh et al., 2018). At low electrolyte concentrations, the potential enters into a Donnan regime where the potential shows a plateau vs. concentration at a fixed concentration ratio between compartments. At high salt concentrations, the potential is related to the induced diffusion potential based on different ionic mobilities of cation and anion, where for single-layer graphene the diffusion coefficients are consistent with the values in bulk solution which is atypical for ion-exchange membranes. TMS is derived for dense, finite width charge-selective interfaces, however the basic features of Donnan and diffusion-dominated regimes are observed for our single-atom thick membrane. This investigation reveals some of the fascinating features of ion-transport across 2D membranes and opens up exciting opportunities for further understanding of transport in such atomistically thin interfaces.

**MONDAY 2:30 pm** - Kings Garden 1

**11b - Developing a new approach to describe ion sorption and transport in Nafion membranes**

Rahul Sujnani (The University of Texas at Austin)\*, Jovan Kamcev (University of California, Berkeley), Eui-Soung Jang (The University of Texas at Austin), Benny Freeman (The University of Texas at Austin), Donald Paul (The University of Texas at Austin)

Ion exchange membranes (IEMs) are widely used in water purification applications, such as reverse osmosis and electrodialysis and are also applied and explored for energy generation applications, such as fuel cells or reverse electrodialysis. IEMs are composed of charged polymers that contain charged moieties bound to the polymer backbone. The presence of these charged groups has significant impact on ion and water transport through these materials and allows for selective permeation of ionic species, making them attractive for the separations required for water and energy applications. However, a detailed understanding of the impact of polymer structure and morphology on ion and water transport properties in IEMs remains largely incomplete. We recently developed a theoretical framework, consistent with thermodynamics, to calculate, and in some cases predict, fundamental ion transport properties in charged polymers. We validated this framework via careful, systematic measurements of water and ion sorption, permeability, and ionic conductivity. We are now extending this framework to Nafion, a perfluorinated sulfonic acid polymer. Nafion has a significantly different chemical structure and morphology than the previous IEMs we have studied. Due to Nafion's exceptional ionic conductivity and robust mechanical and chemical stability, it is considered the benchmark material for fuel cells. The fundamental origins of these unique properties are often debated in the literature. Results for NaCl and MgCl<sub>2</sub> sorption in Nafion show that our framework describes the experimental data remarkably well. Transport measurements were also performed, showing similar behavior reported in the literature, and efforts are underway to model these properties. A key goal of these studies is to identify and elucidate the molecular features of IEMs that can be used to rationally design materials with rapid and selective ion transport.

**MONDAY 3:00 pm** - Kings Garden 1

**11c - Co-transport of neutral solutes in Nafion 117 using In-situ ATR FTIR spectroscopy for multicomponent solution speciation**

Breanna Dobyms (Auburn University)\*, Bryan S Beckingham (Auburn University)

Membranes are widely utilized in many different applications: biological, water treatment, energy production, etc. Transport of species in dense polymeric membranes is described by the solution-diffusion model. For multiple solutes transport behavior has typically been quantified via diffusion cell experiments with ex-situ quantification of downstream concentrations which requires time-consuming aliquot analysis and introduces error through constantly decreasing downstream volume which increases calculation difficulty and introduces hydrostatic pressure issues. Therefore, single component permeability values are generally used to select a membrane for a particular application. Herein, we employ an in-situ attenuated total reflectance Fourier-transform infrared (ATR FTIR) spectrophotometer probe that enables characterization of downstream concentrations for multiple species every minute without the need for aliquotic sampling. We leverage this methodology to investigate emergent transport phenomena for methanol, ethanol, propanol, acetone and combinations thereof through Nafion 117. We find differences between the generally used theoretical selectivity (using single-component permeability values) and the true selectivity (using the multiple component permeability values) of up to 22%. The solution-diffusion model ( $P_i = K_i \times D_i$ ) quantifies changes in permeability,  $P_i$ , to be either thermodynamically driven (solubility,  $K_i$ ) or kinetically driven (diffusivity,  $D_i$ ). Nuclear magnetic resonance (NMR) spectroscopy was used to determine the solubility of the solutes within the membrane via a commonly used adsorption/desorption technique. Once these values are known, the changes in permeabilities/selectivities are shown to be either kinetically or thermodynamically driven. This enables better understanding of transport behavior for multiple components within hydrated, dense polymer membranes.

**MONDAY 3:30 pm** - Kings Garden 1

**11d - Functionalized Nanoporous Ceramic Membranes Towards Low-Cost Electrodialysis**

Gregory M Newbloom (Membrion, Inc.)\*, Ryan Kingsbury (Membrion, Inc.), Rachel Malone (Membrion, Inc.)

The State of California has experienced annual snow pack depletion and persistent drought that is impacting agriculture, industry and day-to-day life. They are not alone as many parts of the world face a fresh water crisis. Interestingly, California, for example, has 38 times more brackish water than fresh water. Electrodialysis is known to be one of the most efficient technologies for purification of brackish water and yet it is often not considered as a leading solution to the fresh water crisis. This is in part due to the cost and performance of the ion exchange membranes (IEM). IEMs suffer from high cost, high resistance, poor durability and other problems. In this presentation, we discuss the design and scale-up of novel, functionalized ceramic IEMs that are ion selective, experience near-zero swelling and are inexpensive at 30% of the production cost of current IEMs. In this work, we investigate the use of a surface-modified inorganic membrane created using sol-gel processing of siloxanes without calcination or sintering. Silica is an advantageous material for membranes because of its excellent durability, extremely low cost and lack of swelling in water. Membrane performance can be tuned by size exclusion (i.e., sub-5nm nanometer pores) and surface functionalization (i.e., silane chemistry) to achieve promising anion and cation-selective performance. Permselectivity and water permeance of these membranes are shown to be superior to an industry standard Neosepta, while area specific resistance has room for improvement. Area-normalized ion exchange capacities and accelerated degradation tests show nearly identical performance between the functionalized ceramic and Neosepta membranes. Design strategies for continued optimization will also be discussed. These promising preliminary results highlight the commercial potential for a new, inexpensive IEM with the potential to elevate the status of electrodialysis as a leading solution to the fresh water crisis.

**MONDAY 4:00 pm** - Kings Garden 1

**11e - Polymerization of counterions in self-assembled, 1 nm pores of lyotropic liquid crystal anion exchange membrane to tune nanopore and ion transport properties**

Michael J. McGrath (University of Colorado at Boulder)\*, Samantha Hardy (University of Colorado at Boulder), Andrew Basalla (University of Colorado at Boulder), Hans Funke (University of Colorado at Boulder), Bryce Manubay (University of Colorado at Boulder), Zhangxing Shi (University of Colorado - Boulder), Douglas Gin (University of Colorado - Boulder), Richard Noble (University of Colorado - Boulder)

The well-defined 1 nm pores of a phase-segregated anion exchange membrane (AEM) made from a cross-linked, self-assembled liquid crystal are functionalized by in-pore polymerization of acrylate-based counter-ions. The resulting anionic polymer is trapped inside the pore and provides a route towards discrete pore modification that can significantly change the material's ion exchange and ion transport properties. After polymer formation inside the pores, the membrane loses its ion exchange capacity but the pore environment remains ionic, as evidenced by water and salt sorption measurements. Single-salt diffusion dialysis chloride/sulfate selectivities are  $> 100$  in both dilute (0.05M) and concentrated (0.5M) solutions for the pore-modified membranes, whereas the unmodified membrane selectivities are  $\leq 1$  at the same concentrations. This work represents an exciting example of an ion selective membrane that relies on mechanisms other than Donnan exclusion, such as size and hydrophobicity, to achieve selectivity. Also, this modification route holds promise in future work to discretely design the pore size of the membrane for targeted nanofiltration separations.

**MONDAY 4:30 pm** - Kings Garden 1

**11f - Quantifying tortuosity and diffusion over multiple scales in ionic and non-ionic polymer membranes**

Louis Madsen (Virginia Tech)\*

Self-organized polymer membranes conduct mobile species (ions, water, alcohols, etc.) according to a hierarchy of structural motifs that can span sub-nm to  $> 10$  microns in scale. In order to understand transport in such materials, our group combines multiple types of dynamics and transport measurements (NMR spectroscopy, diffusometry, relaxation, imaging) with X-ray and neutron scattering, molecular dynamics simulations, and microscopy. We gain perspective on these combined data assisted by theories of porous media, electrolytic transport, and oriented matter. In this presentation, I will focus on the quantification of tortuosity in polymer membranes, meaning the restriction of pathways for diffusion or flow. I will discuss the measurement of tortuosity separately averaged over two distinct length scale ranges - from nanometer to bulk and from micron to bulk. We follow these multi-scale tortuosity values as a function of water uptake and polymer composition. I will present NMR diffusometry measurements of these two quantities in representative systems of hydrophilic-hydrophobic copolymer membranes, including proton-exchange membranes, hydroxide-exchange membranes, and all-neutral membranes. Using such knowledge, our group seeks to give precise feedback on the design of materials for use in, e.g., proton and hydroxide fuel cells, lithium batteries, and water desalination.

**MONDAY 2:30 pm** - Kings Garden 3

**12a - Expanding the chemical palette for reliable chemical separations using molecular simulations and machine learning**

David Sholl (Georgia Institute of Technology)\*, Farhad Gharagheizi (Georgia Institute of Technology), Dai Tang (Georgia Institute of Technology)

The majority of research literature on chemical separations focuses on a relatively small collection of chemicals. In many ways this is appropriate because of the dramatic economic and environmental impacts of these species. The space of possible chemicals, however is vast; Carl Sagan's famous "billions and billions" is many orders of magnitude too small for chemical space. I will discuss early steps towards methods that may eventually allow rapid development of separations using nanoporous materials for a diverse range of molecules drawn from a broad chemical space.

**MONDAY 2:00 pm** - Kings Garden 3

**12b - Diffusion, Reaction, and Network Structure Modeling of Interfacial Polymerization of Polyamide Membranes**

Jeffrey D Wilbur (DuPont Water Solutions)\*, Toni Bechtel (DuPont Water Solutions), Matthew Jansma (DuPont Water Solutions), Steve Rosenberg (DuPont Water Solutions), Dan Arriola (DuPont Water Solutions)

Polyamide membrane chemistry and network structure in reverse osmosis and nanofiltration membranes are a product of simultaneous diffusion and reaction of monomers during interfacial polymerization and are dependent on both feed solution compositions and process conditions. This process has been modeled using various approaches in order to explore the relationship between process inputs, membrane chemical features, and ultimately performance. We present an approach to combine a diffusion-reaction model similar to that described previously by V Freger and a simple statistical model of network structure related to polymerization theory developed by DR Miller and CW Macosko. Predictions suggested by this model are compared with experimental membrane structure data.

**MONDAY 3:00 pm** - Kings Garden 3

**12c - Optimization of Mixed Matrix Membrane Materials for Post-Combustion Carbon Capture**

Janice A. Steckel (U.S. Department of Energy National Energy and Technology Laboratory)\*, Samir Budhathoki (U.S. Department of Energy National Energy and Technology Laboratory), Miguel Zamarripa-Perez (U.S. Department of Energy National Energy and Technology Laboratory), Paul Boone (University of Pittsburgh), Christopher Wilmer (University of Pittsburgh)

Highly selective and permeable membranes have the potential to allow for economically viable, membrane-based post-combustion CO<sub>2</sub> capture. While pure polymer membranes have a long history of usefulness in gas separations, they are characterized by a trade-off between permeability and selectivity known as the Robeson upper limit. Mixed matrix membranes (MMMs) are formed by incorporating inorganic porous nanoparticles, such as metal organic frameworks (MOFs), into a polymer membrane. Some MMMs have been shown to have selectivity and CO<sub>2</sub> permeability that are dramatically improved with respect to the parent polymer. Recently, we demonstrated that computations can accurately describe the performance that is observed when a wide variety of MOFs and polymers are combined in MMMs. In the current work, we use high-throughput atomistic simulations to calculate gas permeability in a large number of MOF structures. Monte Carlo simulations are used to calculate gas solubility and molecular dynamics simulations are used to calculate gas diffusion. These data are combined with experimental data for several polymers to predict the gas permeability of a large number of hypothetical MMMs using a predictive permeation model for the composite material. A multi-stage membrane system for carbon capture was optimized together with the material chosen for the membrane units. A mixed integer nonlinear programming model was used to determine the optimal design and operation of the post-combustion carbon capture plant. The cost of electricity was minimized as a function of plant configuration, process conditions and material properties. This computational screening and optimization study allows us to describe the features of the MOFs and the polymers that contribute to the best membranes, and to optimize the materials together with the process configuration and conditions for membrane-based CO<sub>2</sub> capture.

**MONDAY 3:30 pm** - Kings Garden 3

**12d - Diffusivity in anion exchange membranes under low hydration: A molecular dynamics study**

Dario Dekel (Technion - Israel Institute of Technology), Israel Zadok (Technion - Israel Institute of Technology), Srdan Pusara (Technion - Israel Institute of Technology), Simcha Srebnik (Technion - Israel Institute of Technology)\*

Chemical degradation of cationic groups in anion exchange membranes (AEMs) has been recently shown to be significantly influenced by the hydration level at which the membrane operates. When the AEM is poorly hydrated, the cationic functional sites are more susceptible to attack by the diffusing hydroxide anions. Recent experiments on AEMs functionalized with various quaternary ammonium derivatives have shown significant decomposition of the membranes at low hydration. Using molecular dynamics simulations, we explore the behavior of common quaternary ammonium cations at very low hydration, focusing on solvation of hydroxide and its relation to cation-anion interactions. Diffusivity under different levels of hydration is shown to follow two distinct regimes. Analysis of the hydrogen-bonded water-hydroxide network within the different regimes reveal a unique water-bridged double-hydroxide charged complex that predominates at low hydration. These stable structures are distinct from previously reported structures under hydrated conditions, and presumably disrupt the hydrogen bonded network required for structural diffusion of hydroxide ions through water.

**MONDAY 4:00 pm** - Kings Garden 3

**12e - Modeling of polymer membrane formation via phase inversion by mesoscopic phase-field methods: Investigating the development of structure on multiple scales**

Michael R Cervellere (University of Arkansas/EMD Millipore)\*, Xianghong Qian (University of Arkansas), David Ford (University of Arkansas), Paul Millett (University of Arkansas)

Phase inversion, a process that occurs when a polymer collapses from solution into a thin film upon thermal quenching or exposure to another phase, is the most widely used process for producing porous polymer membranes. Modeling of this process has been mostly limited to the continuum level and empirically-derived parameters, with little theoretical basis to connect the process conditions and important characteristics of membrane microstructure. We have developed a large scale three-dimensional mesoscopic simulation model to examine the dynamics of the phase inversion process and predict the morphology of pore structures that develop within polymer membranes. The computational approach is a phase-field method based on the Cahn Hilliard equation, which incorporates the basic thermodynamic and transport parameters relevant to phase separation in polymer solutions. The thermodynamics of mixing is described by the Flory-Huggins free energy of mixing for binary solutions, and a gradient term is included to govern the formation of interfaces between phases. The transport processes are assumed to be diffusive in nature and are dependent on the local temperature and polymer concentration. We present results for thermally induced phase separation (TIPS) processes using material parameters, polymer volume fractions, and quench rates that are relevant to industrial systems. Integrally skinned membranes can be formed via TIPS and controlling the morphology of the skin layer is of great industrial interest. The model is able to capture the formation of a dense skin layer and changing relevant parameters such as coagulation bath temperature and polymer weight % of the dope has a significant effect on thickness and pore size. This talk will focus on initial results of the Cahn Hilliard model and compare simulated structures and morphologies to current manufactured polymer membrane filters.

**MONDAY 4:30 pm** - Kings Garden 3

**12f - Multiscale Modeling of Gas Permeation Through Poly(Dimethyl Phenylene Oxide) (PPO) and Its Pre-Steady State Polymer Response**

Marielle Soniat (Lawrence Berkeley National Laboratory)\*, Meron Tesfaye (Lawrence Berkeley National Laboratory), Daniel Brooks (CalTech), Nicholas Humphrey (USC), Lien-Chun Weng (Lawrence Berkeley National Laboratory), Boris Merinov (CalTech), William Goddard (CalTech), Adam Weber (Lawrence Berkeley National Laboratory), Frances Houle (Lawrence Berkeley National Laboratory)

In gas separations, glassy polymers are often used because of their high selectivity. However, in applications involving carbon dioxide or other small organic molecules, the interaction between the permeant and the polymer can increase permeability of the membrane over time or at high pressure, known as plasticization. This work reports a combined experimental-theory-multiscale modeling investigation of the transport of two gases, CO<sub>2</sub> and N<sub>2</sub>, through the glassy polymer poly(dimethyl phenylene oxide) (PPO) to better understand the relationship of glassy polymer structure and dynamics with gas transport for both steady and pre-steady state conditions. The multiscale model consists of physically-based coupled reaction-diffusion kinetics and is solved using a stochastic algorithm, which allows for dynamic swelling of the membrane in the presence of CO<sub>2</sub>. The model is validated against experimental data on the pre-steady state and steady state downstream pressure increase over time. The simulations show that polymer response differs for CO<sub>2</sub> and N<sub>2</sub> even at very short times and therefore affects the time-dependent permeation process. The connection between these molecule-polymer interactions and plasticization of the polymer during use will be discussed.

**TUESDAY 9:30 am** - Kings Garden 4

**13a - Scaling mitigation in membrane distillation through electrokinetic mixing**

Unnati Rao (UCLA)\*, Guy Z Ramon (Technion - Israel Institute of Technology), Eric Hoek (UCLA), David Jassby (UCLA)

A major challenge faced by membrane-based desalination processes is the growth of mineral crystals on the membrane surface (scaling). Scaling restricts the flow of water through the membrane and can cause physical destruction of the membrane material. Scaling occurs when supersaturation conditions develop along the membrane surface, a process known as concentration polarization. The depletion of water along the membrane due to its passage to the permeate side leads to the formation of a concentration polarization layer. To mitigate scaling, concentration polarization must be minimized by limiting water recovery, encouraging turbulent conditions and the use of anti-scalants. Here, we report on an energy efficient technology that uses electrokinetic mixing to nearly eliminate calcium sulfate and silicate scaling in membrane distillation. Electrically conductive membranes are prepared by depositing a layer of carbon nanotubes (CNT) on a polypropylene support and crosslinking with polyvinyl alcohol. The application of low potentials (2V cell potential) to the membrane had a dramatic impact on scaling, with the impact being dependent on the frequency of the potential applied. Theoretical calculations reveal that the concentrations of ions along the membrane surface respond rapidly to the applied electrical potentials. We hypothesize that frequent shifts in membrane polarization induce electrokinetic mixing in the stagnant boundary layer and reduce available time for crystal nucleation, shifting the system from rapid heterogeneous nucleation on the membrane surface to slow homogeneous nucleation in the bulk fluid, which nearly eliminated membrane scaling.

**TUESDAY 10:00 am** - Kings Garden 4

**13b - Donnan dialysis desalination with thermolytic salts**

Hanqing Fan (Columbia University)\*, Ngai Yin Yip (Columbia University)

Donnan dialysis (DD) is an ion-exchange membrane (IEM) process that utilizes the Donnan equilibrium principle to drive ion transport. In DD, the IEM separates two solutions with different counterions. Unlike conventional electrodialysis, no external electric current is applied. The IEM allows the transport of counterions in both directions but suppresses co-ion permeation, resulting in the redistribution of counterions until the same equilibrium membrane potential is reached for all different counterions, i.e., co-ions are retained but counterions are exchanged. Here, we proposed a novel desalination technology that couples DD with thermolytic salts and utilizing low-grade heat as energy input. Brackish feed water simulated by NaCl solution and working solution of  $\text{NH}_4\text{HCO}_3$  flow through a cation exchange membrane (CEM) and then an anion exchange membrane (AEM) sequentially. In the CEM cell,  $\text{Na}^+$  in the feed migrates to the working solution chamber while  $\text{NH}_4^+$  permeates in the opposite direction. On both sides, anions are retained. Similarly in the AEM cell,  $\text{Cl}^-$  and  $\text{HCO}_3^-$  are swapped while cations remain. The next result is the substitution of NaCl with  $\text{NH}_4\text{HCO}_3$ . Heating the two outlet streams volatilize the  $\text{NH}_3$  and  $\text{CO}_2$ , thus removing  $\text{NH}_4\text{HCO}_3$  to yield desalinated product water and concentrated brine. The separated  $\text{NH}_3$  and  $\text{CO}_2$  are then recycled to reform the working solution. The concept is experimentally validated by the desalination of brackish water simulated by 100mM NaCl feed to 17mM (i.e., WHO drinking water standard). We further present an analytical model for DD desalination. The results indicate the leakage of co-ions and uncharged species as the major inefficiencies. The research demonstrates a new desalination strategy that utilizes Donnan dialysis with low-grade heat sources, such as waste heat. On a broader perspective beyond desalination, this approach opens up new opportunities to tap low-grade heat for general ion separation.

**TUESDAY 10:30 am** - Kings Garden 4

**13c - Electrically Conductive Membranes as Sensors: Stability, Conductivity, and Sensitivity**

Nan Zhang (McMaster University), Amin Halali (McMaster University), Charles-François de Lannoy (McMaster University)\*

Polymeric membranes are susceptible to various forms of fouling including organic, colloidal, and biofouling, as well as mineral scaling. The onset of fouling is most often monitored by changes in transmembrane pressures drop. The type of fouling is elucidated from feed water composition and in destructive membrane autopsies. The ability to monitor membrane fouling in-situ would enable immediate and finely tuned anti-fouling responses. This work focuses on electrically conductive membranes as fouling sensors. The presentation will also provide an overview of our recent conductive membrane chemistries, their stability, electrical conductivity, and production of flat sheet and hollow fiber configurations. To develop fouling sensors on membranes, we used electrochemical impedance spectroscopy (EIS) on the surface of electrically conductive membranes to precisely measure the onset of surface fouling. We fabricated an electrochemical cell containing an electrically conductive membrane as the working electrode, a graphite electrode as the counter electrode, and a NaCl solution as electrolyte. Conductive membranes were fabricated by coating PES and PVDF flat sheet and hollow fiber membranes with single-walled/double-walled CNT (SW/DWCNT) solutions. Membrane fouling was simulated by pressure depositing layers of latex beads onto the surface of the membrane. Changes in membrane permeance were used to correlated the extent of latex fouling, i.e. different thicknesses of latex fouled layers caused reductions in membrane permeance. These small changes in latex coverage on membranes were resolved with EIS quantified as Nyquist plots. Direct mechanistic interpretations of impedance impacts are possible and we have developed relevant equivalent circuits to model these systems. This research demonstrates that electrically conductive membranes are an ideal platform to use EIS to sense the onset and development of surface fouling.

**TUESDAY 11:00 am** - Kings Garden 4

**13d - Electrocatalytic Membrane Reactor-based Integrated Processes for Landfill Leachate Treatment**

Jianxin Li (Tianjin Polytechnic University)\*, Hong Wang (Tianjin Polytechnic University), Junhao Ding (Tianjin Polytechnic University)

Treatment of nanofiltration (NF) retentate from landfill leachate is a significant challenge due to its poor biodegradability and high toxicity. One attractive potential alternative is to apply a chemical oxidation processes for pretreatment to convert the initially persistent organic compounds into more biodegradable intermediates, which could then be treated with a biological oxidation process at a considerably lower cost. This study reports the development of a novel integrated process, i.e. Fenton-electrocatalytic membrane reactor (ECMR)-biological aerated filter (BAF) process for the treatment of NF retentate from landfill leachate. The Fenton and ECMR processes were applied prior to the biological process to enhance the biodegradability of the leachate, making it suitable for the subsequent biological process. The results showed that the chemical oxygen demand (COD) removal rate of the effluent obtained from the Fenton process under the conditions of pH=3, molar  $[H_2O_2]/[Fe^{2+}]$  ratio of 2:1 ( $H_2O_2$  dosage of 180 mmol/L) was up to 64.6%. Simultaneously, the biochemical oxygen demand (BOD<sub>5</sub>) increased from 62 to 138 mg/L. The effluent from the Fenton process was then treated with the ECMR process under the operating conditions: an operating voltage of 2.0 V and a residence time of 10 min. The COD removal rate reached 21.3% and the ratio of BOD<sub>5</sub> to COD (B/C) increased from 0.05 to 0.38, indicating that is biodegradable. After 48 hours of BAF treatment, the COD of the effluent declined to 88 mg/L and the total of chroma removal rate reached 99.5%. All the contaminants in effluent can satisfy Discharge Standard of China. In sum, our research opens a new avenue for landfill leachate treatment without concentrates.

**TUESDAY 11:30 am** - Kings Garden 4

**13e - Nitrogen and Phosphorus Recovery from Agricultural Wastewater Effluents - Role of Electrically Conductive Membranes**

Avner Ronen (Temple University)\*, Kartikeya Kekre (Temple University)

Nitrogen and phosphorus are essential elements needed for agricultural crop fertilization, used in increasing quantities in order to feed an ever-growing population. Production of both nitrogen and phosphorus fertilizers is energy intensive and their demand is expected to increase in the coming decades due to changes in human population, diets, and agricultural practices. Agricultural wastewater from livestock (AWL) farms contains high concentrations of nitrogen and phosphorus in addition to organic loads. Currently, conventional wastewater treatment plants are unable to remove such high concentrations, which require complex treatment stages and reduce the efficiency of the treatment. An important strategy to mitigate phosphorus and nitrogen scarcity is to recycle them from waste streams back into agricultural production. Our research shows the ability of P and N recovery from concentrated and diluted solutions ( $1-100 \text{ mg L}^{-1}$ ) of synthetic AWL. The recovered P and N are in the form of Struvite which is considered an "eco-friendly" fertilizer. The recovery is based on an electrochemical reaction near an electrically conducting ultrafiltration membranes (ECM). The electrochemical reduction of dissolved oxygen and water molecules generate a local pH gradient in the close vicinity of the electrode. The pH near the cathode increases, leading to nucleation and growth of Struvite and, importantly, high yield with no chemical additives. As the recovery process utilizes permeate to control mass transfer, diffusion limitations are eliminated, leading to a significant increase in reaction rates and removal ratio. In terms of collecting the recovered Struvite, our ECMs have pores in the range of 10-100 nm which are significantly smaller than the size of Struvite particles, therefore, Struvite solid particles which are filtered by the ECM accumulate on the membrane's surface, to be collected by a pressurized backwashing process or simply blocking the permeate flux.

**TUESDAY 12:00 pm** - Kings Garden 4

**13f - Simulations of Highly Selective Separations Based on Electromigration**

Merlin Bruening (University of Notre Dame)\*, Andriy Yaroshchuk (Polytechnic University of Catalonia), Mykola Bondarenko (National Academy of Sciences of Ukraine), Chao Tang (University of Notre Dame), Muhammad Ahmad (University of Notre Dame)

In ion transport through membranes, spontaneous or applied electric fields give rise to electromigration that sometimes leads to extraordinary selectivities, particularly when electromigration opposes convective transport. This presentation will explore electric field-induced selectivities in both ion-exchange membranes and in membranes that contain highly charged nanopores. In diffusion dialysis through an anion-exchange membrane, the  $\text{Cl}^-/\text{SO}_4^{2-}$  selectivity increases from 1.3 to 13 on going from a source-phase concentration of 0.005 M to 0.1 M. Simulations suggest that this occurs because electromigration disproportionately decreases  $\text{SO}_4^{2-}$  transport due to its 2-charge and high concentration in the membrane. With diffusion dialysis of 0.1 M KCl, 0.1 M  $\text{MgCl}_2$  through a cation-exchange membrane, concentration profiles and electromigration can even lead to negative  $\text{Mg}^{2+}$  fluxes with low ion concentrations in the receiving phase. During application of an electrical current through a membrane containing micro and nanoporous regions, trace-ion accumulation in the microporous layer should vary greatly with the ion diffusion coefficient to allow selective preconcentration of specific ions. The charged nanopores exclude coions (ions with the same charge as the nanopore walls) to deplete the region next to the nanopores of the dominant (high-concentration) salt and give rise to high local electric fields. Trace ions accumulate in the depletion region because convection moves them toward the nanoporous interface, but the opposing electromigration is greatest near the interface. When the trace-ion diffusion coefficients is half of the corresponding value for the dominant salt, calculated preconcentration factors reach 150. Much larger enrichment factors appear for divalent ions due to their relatively low diffusion coefficients.

**TUESDAY 9:30 am** - Ballroom 3

**14a - Oil drop behavior on model nanofiltration membrane surfaces under conditions of hydrodynamic shear**

Emily Tummons (Michigan State University), Charifa Hejase (Michigan State University)\*, Zhefei Yang (University of Massachusetts Amherst), Jia Wei Chew (Nanyang Technological University), Merlin Bruening (University of Notre Dame), Vlad Tarabara (Michigan State University)

Large volumes of oily wastewater are produced in various industrial operations. Membrane filtration is the most cost-effective technology capable of removing oil droplets smaller than 10  $\mu\text{m}$ , often a prerequisite for meeting environmental regulations. However, membrane fouling by oil limits the broader acceptance of this technology. Despite extensive studies, mechanisms of membrane fouling by emulsified oil remain poorly understood. The blocking laws do not apply to deformable particles such as oil droplets. Conditions that lead to oil accumulation into compressible cakes or formation of contiguous films also remain unclear. In the present work, we investigated the impacts of anionic surfactant and salt on oil droplet adhesion to model nanofiltration membranes. The Direct Observation Through the Membrane (DOTM) technique was employed to visualize oil drop deposition and adhesion to polyelectrolyte multilayers (PEM) with opposite surface charges, supported by Anopore ultrafilters. Hexadecane-in-water emulsion was stabilized by sodium dodecyl sulfate (SDS) and had a controllably varied concentration of monovalent ( $\text{Na}^+$ ) and divalent ( $\text{Mg}^{2+}$ ) counterions. Quartz crystal microbalance and FTIR analyses showed that PEM coatings were stable when exposed to SDS indicating their suitability for nanofiltration of surfactant-stabilized emulsions. Visualization by DOTM was complemented by a force balance analysis to predict the critical size for a droplet that would be swept off the surface by the crossflow drag. The results indicate that interfacial tension, electrostatic droplet-droplet and droplet-membrane interactions, and membrane's affinity for oil together govern attachment of oil drops to membrane surfaces. Crossflow-controlled coalescence was promoted under conditions of moderate affinity between oil drops and the polyelectrolyte-coated surface when the drops could reach a critical size and be removed by the crossflow shear prior to forming a contiguous surface film.

**TUESDAY 10:00 am** - Ballroom 3

**14b - A case study review of the application of reverse osmosis membranes for water treatment and reagent recovery at mining and mineral processing operations**

Chris Biederman (Hatch)\*, Jeffrey Cobbleddick (Hatch)

Water is an integral part of mining and mineral processing. It is used in almost every major ore processing stage and without ready access to it, the recovery of valuable minerals becomes prohibitively expensive or altogether not possible. Treating mine water presents a unique challenge as no two mine sites have the same water chemistry. Water chemistry at a mine site can be influenced by variations in the geochemical make-up of the ore body, the volume and quality of ground water seepage that is collected, any chemicals that are added to improve mineral recovery, and seasonal precipitation and run-off. Mine waters often contain scale-forming ions - such as calcium, magnesium, manganese, iron, sulfate, silica, and alkalinity - at exceedingly high concentrations. Many of these ions can cause significant issues for a membrane water treatment plant if not thoroughly considered during the design stage. This presentation will show the variations - sometimes extreme - in water chemistry between mine sites in different geographic regions of the world. This will be followed by three case studies to demonstrate the wide variation in potential uses for membranes in a mining environment and some of the pitfalls to avoid. The first case study will review the use of spiral wound UF and RO membranes to recover calcium thiosulfate reagent at a gold mine. The importance of stable pre-treatment, membrane selection and membrane flow control will be discussed. The second case study will demonstrate the challenges with retrofitting a reverse osmosis system to a brownfield water treatment plant at a nickel-copper mine. Challenges associated biological and colloidal sulfur fouling downstream of an advanced oxidation process will be presented. The final case study will be the review of a conceptual design for a greenfield reverse osmosis mine water treatment plant at a lithium mine that is projected to have water with 1 to 2 g/L of boron.

**TUESDAY 10:30 am** - Ballroom 3

**14c - Self-Cleaning Nanocomposite Membranes with Phosphorene-Based Pore Fillers for Water Treatment**

Joyner Eke (University of Kentucky)\*, Isabel Escobar (University of Kentucky)

Photocatalytic membrane processes generate oxygen-reactive radicals under irradiation by light that could degrade pollutants in feed solutions. Phosphorene is a two-dimensional material made by exfoliating black phosphorus, a monotypic van der Waals crystal. Unlike other common two-dimensional materials, under light irradiation, phosphorene can generate reactive oxygen species (singlet oxygen, hydroxyl radicals and superoxide radicals). In this study, we exfoliated black phosphorus to synthesize phosphorene. Then immobilized the phosphorene nanomaterial into the membrane (sulfonated poly ether ether ketone and polysulfone blend). Studies were done under ultraviolet light irradiation. The dye, methylene blue was used as feed solution. Membranes were comprehensively characterized before and after modification. Results obtained showed enhanced flux recovery for the phosphorene modified membranes. Fluorescent studies also revealed lower coverage of methylene blue on these membranes as compared to the unmodified membranes. Mechanism of photocatalysis will be investigated and reaction equations proposed

**TUESDAY 11:00 am** - Ballroom 3

**14d - Optimization of nanofiltration process for treating industrial wastewater of time-varying composition**

Salman Alizadeh Kordkandi (McMaster University); Ryan LaRue (McMaster University)\*; Abhishek Premachandra (McMaster University); Jacob Sitko (McMaster University); David Latulippe (McMaster University)

Industrial wastewater (IWW) contains a complex mixture of components that depends on the facility where it is generated (e.g. slaughterhouse, brewery, pulp & paper plant). While many studies have focused on using membranes to treat IWW from a single facility, there have been no studies that addressed the significant challenge faced by specialized treatment plants that are designed to receive shipments of IWW from many different facilities. The time-varying composition of the influent to these treatment plants is quite considerable, yet the composition of the effluent must consistently meet the mandated discharge criteria. In this study, we have focused on using nanofiltration (NF) membranes to remove the organic components in IWW that contribute to the chemical oxygen demand (COD) parameter. In collaboration with a local company, we have collected over 80 samples of the influent IWW to their facility and analyzed them using a liquid-liquid extraction process and gas chromatography-mass spectroscopy (GC-MS) to identify the most common chemical compounds. We then used a subset of 15 of those samples, that had considerable variation in chemical composition, and evaluated the performance of various commercial flat-sheet NF membranes (five were polyamide and one was polypiperazine-amide) from three different companies. We have found a significant difference in the performance (both volumetric throughput and quality) for those NF membranes with the same IWW sample and across different IWW samples. For example, the total reduction in COD varied from 30% to 80% for one particular IWW sample. Using the same GC-MS based analysis of the filtrate samples, we saw significant variation in the rejection of individual compounds. For example, the rejection of butanoic acid varied from 0 to 90%. We are currently working to develop a fundamental understanding of the relationship between the physico-chemical properties of the membranes and the filtration performance.

**TUESDAY 11:30 am** - Ballroom 3

**14e - Adsorptive and Reactive Membranes for Remediation of PFOA, Chloro-organics, and RCRA Metals from water**

DB Bhattacharyya (University of Kentucky)\*, Hongyi (Derek) Wan (University of Kentucky), Anthony Saad (University of Kentucky), Md. Saiful Islam (University of Kentucky), Ashish Aher (University of Kentucky), Rollie Mills (University of Kentucky), Lindell Ormsbee (University of Kentucky), Evan Hatakeyama (Chevron)

The contamination of aquifers by toxic metals and organic compounds is a widespread problem. Traditional membranes, such as RO, NF, UF provide many successful water applications. But incorporation of nanostructured materials with responsive and tunable properties in microfiltration type membranes has added immense value in through adsorptive separations and water detoxification in the area of pollutant remediation. The use of macromolecules in microfiltration membrane pores, such as, poly-acrylic acid (PAA) for pH responsive behavior, and Poly-N-isopropylacrylamide (PNIPAm) for temperature responsive behavior, provides tunable water permeability, and a platform for pollutant sorption/desorption and immobilization of pollutant degradation catalyst. In addition, we have created high capacity adsorptive membranes with SH and other functional groups in membrane pores for RCRA metals (such as, Hg) removal. The use of temperature responsive membranes (such as, PNIPAm) allow adsorption/desorption of organics by using TSA (temperature swing sorption/desorption) approach. Perfluorinated compounds (PFCs) such as Perfluorooctanoic acid (PFOA) and Perfluorooctane sulfonate (PFOS) have gained much attention due to their environmentally persistent nature. PNIPAm exhibits a phase transition from a hydrophilic state to a hydrophobic state at its LCST of 32 C. With PNIPAm hydrogel, initial PFOA sorption rate of about 28 mg/g gel/h was observed above LCST, and desorption below LCST. The presentation will water applications in three areas: (1) PFOA adsorption/desorption kinetics below above LCST by PNIPAm hydrogels, and in-situ polymerized NIPAm in membrane pores, (2) Chloro-organic degradation in PAA functionalized PVDF membranes containing Fe/Pd nanoparticles, (3) high capacity sorption of toxic metals (Hg) with membrane pores functionalized with SH groups. This research is funded by NIEHS-SRP, NSF-EPSCOR program, and Chevron Corp.

**TUESDAY 12:00 pm** - Ballroom 3

**14f - Selective separation of mono- and di-valent cations in electrodialysis during brackish water desalination: bench and pilot-scale studies**

Xuesong Xu (New Mexico State University)\*, Pei Xu (New Mexico State University), Guanyu Ma (New Mexico State University)

Selective separation of mono- and multi-valent ions has important applications in water reuse, desalination, and salt production. Innovative monovalent permselective cation-exchange membrane CR671 was developed by modifying the normal grade membrane CR67 with polyethyleneimine coating. Bench- and pilot-scale electrodialysis experiments were conducted at a brackish groundwater desalination facility to investigate desalination performance and ion permselectivity using the CR671 and CR67 under different operating conditions. Both normal grade (CR67 and AR204) and selective (CR671 and AR112B) membranes achieved same desalting efficiency. Na-selectivity in terms of relative transport number using sodium as standard ion was affected significantly by current density and linear velocity for the normal grade membranes while the selective membranes exhibited relatively stable good Na-selectivity. The Na-selectivity of the CR671 was demonstrated up to 9 and 5 times better than the CR67 during pilot- and bench-scale electrodialysis, respectively. Hydraulic retention time and electrodialysis stack staging had minor impact on Na-selectivity at high current density. With the same hydraulic conditions, overall desalination behavior and ion permselectivity were highly comparable between bench- and pilot-scale electrodialysis. It infers that bench-scale testing results can be used to simulate and project desalination performance and ion selectivity of pilot- and potentially full-scale electrodialysis applications.

**TUESDAY 9:30 am** - Ballroom 4

**15a - Membrane solvent recovery in edible oil industry**

Petrus Cuperus (SolSep BV)\*, Ingrid Wienk (SolSep BV), Pieter Vandezande (VITO), Marco Pipolo (Bunge), Jan Kolijn (TUSTI), Will Fuchten (MTSA)

OSN technology is very well fitted for partial recovery of organic solvents in existing distillation installations. The past four years Solsep has been heavily involved in trialing such membranes in the industrial environment of such solvent: in particular acetone. In a last term of 2 years polymeric and ceramic membranes are tested for their stability, performance and window of operation. Currently used distillation/evaporation can be 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. In this area membrane permeation and separation as well as ease of evaporation and energy costs play a role. Inside-industry work has been focused on recovery of oil-acetone mixtures (oil: palm, shea). For operation on the long run clean-in-place procedure were evaluated. More than 2 years of in-industry piloting - NF with evaporation- has been done and will be addressed in the presentation. For economic evaluation extensive modeling work-backed-up by experimental work- suggest PBTs for different scenarios for implementation of the technology. We will discuss work on the removal of solvents and possible use in industry. Acetone-vegetable oil processing is presented in the development from lab-scale to long term pilot-scale executed -in "real life".

**TUESDAY 10:00 am** - Ballroom 4

**15b - Molecular Design of Polymeric Membranes for Organic Solvent Recovery**

Tai-Shung Chung (National University of Singapore)\*

Organic solvent nanofiltration (OSN), also known as solvent resistant nanofiltration (SRNF), is an emerging liquid separation method with substantial applicability in pharmaceutical, food and petrochemical industries. OSN not only aims to separate solutes or compounds with a molecular weight (MW) of 200-1000 g/mole from organic solvents but also to recycle the costly organic solvents used in related industries. As a result, the development of OSN technology may potentially reduce medicine costs and CO<sub>2</sub> emission. The solvent resistant nanofiltration membrane is the core of OSN processes which ideally should possess a pore size of 0.5-2.0 nm for an effective separation and purification of valuable solutes and recycling of organic solvents. In this presentation, we will introduce our recent efforts on membrane development for OSN systems. Various material and fabrication strategies to enhance membrane performance will be discussed.

**TUESDAY 10:30 am** - Ballroom 4

**15c - Epoxy-based solvent resistant nanofiltration membranes prepared through phase inversion**

Maarten Bastin (KU Leuven)\*, Jasper Raymenants (KU Leuven), Ivo Vankelecom (KU Leuven)

A novel method has been successfully developed for the synthesis of solvent resistant nanofiltration (SRNF) membranes. The bulk chemistry of epoxy curing via ring-opening reactions has been applied in a phase inversion process, resulting in membranes with excellent solvent stability and water permeability, making them particularly suitable for the treatment of solvent/water mixtures. Several epoxy monomers were selected based on their size and number of epoxide functional groups and different amines were chosen as curing agent, based on their chemical composition, length and reactivity. Both the epoxy monomer and amine were dissolved in DMSO and left to react which, due to the increased number of crosslinks in the matrix resulted in an increase in viscosity. The solutions viscosity was monitored as a function of time and related to the reaction kinetics of the epoxy-amine curing system. Integrally skinned asymmetric membranes were prepared via phase inversion. The membranes were characterized via SEM, ATR, contact angle measurements and filtration experiments with different solvent water mixtures and dyes of various charges and size. Depending on the type of epoxy monomers and concentration, a range of membranes could be prepared, with NF properties (rose bengal retention of 95% in DMF/water and permeance of 1 - 3 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>) or UF properties which in their turn can be used as support for full epoxy thin film composite (TFC) membranes. In this case, on top of the UF-epoxy supports, an epoxy-cured top-layer can be added via interfacial polymerization, resulting in an ultrathin top-layer on an UF-support layer, all in the same poly(epoxy ether) material, giving the overall benefit of having the same swelling behaviour in similar chemical environments which decreases the chance of defects.

**TUESDAY 11:00 am** - Ballroom 4

**15d - Nanoporous Graphene Membranes for Organic Solvent Nanofiltration**

David Cheng (MIT)\*, Rohit Karnik (MIT)

The separation of fine chemicals and pharmaceuticals from organic solvents during chemical processing is currently extremely energy-intensive due to the use of solvent evaporation for separation, which also prevents re-use of solvent leading to significant costs. Membranes that can easily handle solvents and separate them from small molecules, e.g. fine chemicals/active pharmaceutical ingredients, have the potential to significantly reduce energy consumption and enable solvent recovery and re-use, thereby lowering the energy costs and making chemical manufacture more environment-friendly. However, versatile membranes that are compatible with a range of solvents and also have the required selectivity are not readily available. Based on our recent success in developing nanoporous graphene membranes for aqueous and gas separation based on size-exclusion, we show in this work the development of nanoporous graphene membranes for performing pharmaceutical/fine chemicals separations from solvents. With its atomic thickness, high mechanical and chemical stability, and the ability to sustain selective, sub-nanometer pores in its rigid lattice, nanoporous graphene has tremendous potential as a material for next-generation membranes, yet little is known about transport of solvent and small molecules across nanoporous graphene. We reveal peculiar solvent and small molecule transport behaviors through nanoporous graphene and demonstrate size-based separation in solvents, potentially opening a new arena for replacing distillation with more efficient membrane separations.

**TUESDAY 11:30 am** - Ballroom 4

**15e - OSN Technology in Petrochemical Industry: Looking Back, Looking Forward**

Dhaval Bhandari (Exxon Mobil), JR Johnson\* (Exxon Mobil)

Organic mixture separations are considered to be significantly more challenging than aqueous and gas separations due to the combination of high chemical, physical and often thermal constraints put on the membranes. ExxonMobil and Grace successfully commercialized the first large scale OSN technology, Max-Dewax™ for lube oil dewaxing in 1998. Key technical features of the technology that led to its successful commercial operation are highlighted. Over the last 10 years, homogenous catalyst recovery and solvent purification applications have also been developed and deployed. Organic liquid separation membranes are still considered 'emerging' while its cousin - gas separation membranes have enjoyed a relatively broader success in the petrochemical industry. Critical challenges in OSN commercialization are discussed and identified to be somewhat contrary to commonly held beliefs. The advent of dual challenge\* is especially relevant in petrochemicals manufacturing where thermal processes still account for ~45% of energy consumption. Key development needs are identified for the next generation of OSN/OSRO technology to make an impact in this space. \*dual challenge - ensuring the world has access to affordable and reliable energy supplies to support prosperity while reducing environmental impacts - including the risks of climate change. Weblink - <https://corporate.exxonmobil.com/en/energy/energy-outlook>

**TUESDAY 12:00 pm** - Ballroom 4

**15f - Enabling Organic Solvent Nanofiltration and Reverse Osmosis using Ceramic Supported TFC Membranes**

Jeffrey R McCutcheon (University of Connecticut)\*, Lingling Xia (University of Connecticut), Marcus Weyd (Fraunhofer Institute for Ceramic Technologies and Systems IKTS), Mi Zhang (University of Connecticut)

We report on the performance of a ceramic supported polyamide thin film composite (TFC) membrane for organic solvent nanofiltration (OSN) and organic solvent reverse osmosis (OSRO) applications. The membranes are made by conventional formation of an aromatic polyamide selective layer directly onto a ceramic ultrafiltration membrane. The polyamide has demonstrated resistance to solvents while retaining molecular selectivity and the ceramic support is stable in most any solvent. We explore the use of different solvents and different dyes to probe differences in polyamide selectivity performance between different solvents and dyes. We also explore the use of these membranes in separating miscible solvent pairs via organic solvent reverse osmosis. In all, we note that certain solvents can alter the polyamide permselective properties and that these effects seem to be linked to the solvent's Hansen solubility parameter of the solvent. We also note that while these polymers demonstrate some level of selectivity with a particular solvent (i.e. "solvent activation"), changing from one solvent to another may result in unpredictable selectivity and permeance performance.

**TUESDAY 9:30 am** - Kings Garden 3

**16a - Responsive CNT Composite Membranes for Protection Against Chemical Warfare Agents**

Melinda L Jue (Lawrence Livermore National Laboratory)\*, Chiatai Chen (Cornell University), Yifan Li (MIT), Eric Meshot (Lawrence Livermore National Laboratory), Ngoc Bui (Lawrence Livermore National Laboratory), Rong Zhu (MIT), Myles Herbert (MIT), Sei Jin Park (Lawrence Livermore National Laboratory), Steven Buchsbaum (Lawrence Livermore National Laboratory), Kuang Jen Wu (Lawrence Livermore National Laboratory), Timothy Swager (MIT), Francesco Fornasiero (Lawrence Livermore National Laboratory)

Stimuli responsive materials have many diverse applications in areas such as drug delivery, sensors, dynamic surfaces, and advanced textiles. In the field of responsive fabrics, high breathability and fast response to external stimuli are desired to combine comfort with "smart" functions. Materials of this type could be utilized, for example, to create protective garments that selectively respond to chemical threats without adding undue physiological stress to the user, thereby prolonging the safe wear. In this work, vertically-aligned single-walled carbon nanotubes (SWCNT) are used to create exceptionally breathable and protective composite membranes. Autonomous, smart response to environmental chemical threats is achieved thanks to an engineered copolymer layer grafted to the surface of the SWCN membranes, which collapses in the presence of organophosphate chemical threats to effectively block their transport through the membrane. This response is local and can be reversed with a simple base treatment. Moisture vapor transport rates that rival commercial breathable fabrics coupled with the ability to block both biological (by size sieving) and chemical threats make these membranes promising materials for next-generation protective garments for military, first responders, and medical personnel.

**TUESDAY 10:00 am** - Kings Garden 3

**16b - Highly Efficient Dimethyl Ether Production from CO<sub>2</sub> Hydrogenation in a Dehydration Membrane Reactor**

Huazheng Li (Rensselaer Polytechnic Institute)\*, Fanglei Zhou (Rensselaer Polytechnic Institute), Qiaobei Dong (Rensselaer Polytechnic Institute), Shoujie Ren (Missouri University of Science and Technology), Xinhua Liang (Missouri University of Science and Technology), Naomi Klinghoffer (Gas Technology Institute), Shiguang Li (Gas Technology Institute), Miao Yu (Rensselaer Polytechnic Institute)

As an important industrial intermediate, Dimethyl Ether (DME), can also be used as a promising clean fuel in various ways. Traditionally, DME is produced either through methanol dehydration or a couple of consecutive reactions directly from syngas. However, the yield of DME is low, limited by the equilibrium, in both processes. In order to increase the DME yield, a novel catalytic membrane reactor to remove the produced water in-situ from the reaction system will be beneficial. In this study, a highly water selective and permeable NaA membrane, prepared on ceramic hollow fibers by an improved seeding method, was applied in a membrane reactor for DME synthesis directly from CO<sub>2</sub> hydrogenation over bifunctional catalysts (CZA/HZSM-5) at challenging conditions (temperature from 220 to 260°C and pressure from 300 to 500 psig). Current results showed that much higher CO<sub>2</sub> conversion (up to 73.4%) and DME yield (up to 54.5%) than those obtained in traditional packed bed reactor were achieved. These results solidly indicate that limitation of equilibrium have been successfully overcome, resulting from the timely and effective water in-situ removal from the reaction system by NaA membrane. Effects of mass ratio of CZA and HZSM-5 catalysts, catalyst mass per membrane area, gas hourly space velocity, catalysts gradients, etc, on catalytic reaction performance and catalyst stability were also intensively investigated.

**TUESDAY 10:30 am** - Kings Garden 3

**16c - Poly-methacrylic acid Functionalized Membranes with Incorporated Reactive Pd/Fe Nanoparticles: Lab Scale to Groundwater Remediation Applications**

Hongyi (Derek) Wan (University of Kentucky)\*, Md. Saiful Islam (University of Kentucky), Nicolas Briot (University of Kentucky), Anthony Saad (University of Kentucky), Lindell Ormsbee (University of Kentucky), DB Bhattacharyya (University of Kentucky)

The detoxification of chlorinated organics, such as trichloroethylene (TCE) and polychlorinated biphenyl (PCB), in groundwater is an important area. With incorporated catalytic Pd/Fe particles, the functionalized commercial MF membrane modules can be used in the dechlorination treatment of groundwater. Membrane functionalization was achieved in both commercial flat-sheet PVDF membranes and spiral membrane modules. The Pd/Fe nanoparticles were synthesized inside the pores of membrane through in situ reduction after ion-exchange with carboxylate groups (methacrylic acid (MAA) was polymerized inside the pores). The MAA prevents nanoparticle agglomeration and metal ion loss. It also entitles the commercial membranes a pH-responsive behavior in the permeability: a 30-fold decrease was found when the pH increase from 2.3 to 10.5 (542 LMH/bar at pH 2.3). The reactive membranes were tested in the treatment of lab synergic PCB and field groundwater (collected from a Superfund site, which includes TCE, carbon tetrachloride, etc.). At 2.2 s residence time, above 90% of chlorinated organic species (10-1000 ppb level) in the groundwater were dechlorinated in the convective flow mode. Advanced characterization methods, such as FIB, EELS and XPS were applied to quantify particle size and distribution at the entire depth of the membrane pores. The depth profile of the membrane indicates that particle size was uniform inside membrane pores ( $24\pm 6$  nm) but slightly smaller than those nanoparticles located on the surface ( $39\pm 9$  nm). Furthermore, the use of TEM and XRD enables the calculation of Pd monolayer coverage on the Fe surface. The effects of Pd surface coverage and particle compositions on the  $H_2$  production (Fe corrosion in water) and corresponding dechlorination rate were evaluated to find the optimal Pd content for the dechlorination. This research is supported by the NIEHS-SRP grant P42ES007380. Partial support is also provided by NSF KY EPSCoR grant (Grant no: 1355438).

**TUESDAY 11:00 am** - Kings Garden 3

**16d - Investigation of a smart electrically responsive ultrafiltration membrane**

Chia Miang Khor (UCLA)\*, David Jassby (UCLA)

Stimuli responsive membranes that enable the smart control of substances flowing through can be enticing as alternative materials for water purification. These materials are capable of conformational changes when exposed to external stimuli such as temperature, pH, electric fields, and electrolyte concentrations. Membrane rejection properties can thus be tailored and facilitate membrane cleaning. Among the different types of external stimuli, electrical signals would have the most plausible prospect, due to the rapid nature of their application and the fact that the stimulus can be delivered through the membrane itself without the need to change the feed stream. In this work, a relatively environmentally benign method, surface initiated electrochemically mediated atom transfer radical polymerization (SI-eATRP), was employed for the surface modification of a carbon nanotube-coated ultrafiltration membrane with an anionic polymer. The resulting membrane was electrically responsive with tuneable pore sizes. Complete release or retention of dextran molecules with molecular weight 12,000 could be achieved through voltage reversals. This was accompanied by considerable changes in water flux through the membrane. Electrostatic repulsion between the grafted polyanionic brushes and charged species in the water was exploited with the application of different voltages to induce conformational changes of the polymer brushes and thus rejection of certain contaminants.

**TUESDAY 11:30 am** - Kings Garden 3

**16e - Catalytic Membranes for Groundwater Treatment**

Alexander J Sutherland (McMaster University)\*, Charles-François de Lannoy (McMaster University)

Zero Valent Iron (ZVI) has received extensive scientific interest for its ability to reduce highly toxic chlorinated organic contaminants (COCs) present in groundwater. The development of Zero Valent Iron nanoparticles (nZVI) has been proven to enhance reactivity as a result of increased surface area. Despite its remarkable potential to remediate COCs, nZVI faces challenges to its reactivity due to particle aggregation and an inability to selectively reduce desired contaminants over other compounds in solution. The goal of this project is to develop a permeable membrane surface composite that allows for the stabilization of nZVI nanoparticles to reduce chlorinated contaminants in the feed. Various conductive materials have been investigated as stabilizers and scaffolds for conducting current to regenerate nZVI reactivity. The results of this project have shown that Carbon Nanotubes (CNTs) can be used as a conductive network to stabilize nZVI to mitigate aggregation, channel electrons to support nZVI as a catalyst, and act as an electrode for electrochemically reducing COCs alongside a graphite counter electrode. By applying a -2V potential to a surface layer of CNT-stabilized nZVI on a Polyethersulfone microfiltration support membrane, model contaminant solutions of 0.25 mM Methyl Orange (MO) can be entirely degraded within three-hour batch tests. This is a marked improvement over membrane electrodes that utilize CNTs alone, which achieve only 70% degradation with the same experimental parameters. Using microfiltration membranes and facilitating the removal through the application of a low voltage presents significant advantages over conventional membrane separation. Firstly, eliminating the requirement of nano-scale pores possessing high trans membrane pressure gradients to accomplish the separation. Secondly, these membranes produce a waste stream of completely degraded contaminants, rather than a concentrated contaminant retentate.

**TUESDAY 12:00 pm** - Kings Garden 3

**16f - Plasmonic membrane catalytic activation of peroxide for quantized oxidation via residence time control**

Hao Tang (University of Washington), Guozheng Shao (University of Washington), Bruce Hinds (University of Washington)\*

Many industrial oxidation processes based on peroxide, have a difficulty of over oxidation in homogeneous solution principally due to faster oxidation rates of already oxidized species and high statistical probability of secondary oxidation near the completion of reaction. Ideal for stepwise oxidation is to limit the residence time of target molecule in a reaction zone to allow for single (or quantized) reaction events. This can be achieved in a membrane geometry where catalyst along a pore length and set flow velocity can precisely control residence time for oxidation. It is also known that Au nanoparticles can catalytically activate peroxide under light irradiation due to the formation of concentrated surface plasmon electric fields and thus hypothesized to be present in nanoporous planes. A plasmonic membrane was synthesized by evaporation of 25 nm thick Au films onto pore entrances anodized aluminum oxide membranes (AAO) with pore diameters of 20-200nm. This allowed solutions of peroxide, benzene, methyl blue to flow through membrane and interact with Au surface plasmon upon exit of the membrane. Under light illumination of 10-100 mW/cm<sup>2</sup>

quantum efficiencies (photon/peroxide radical) of 200-800% were seen, indicating a mechanism of field induced activation of peroxide compared to a hot electron injection mechanism. Dye and benzene to phenol oxidation are demonstrated.

**TUESDAY 9:30 am** - Kings Garden 5

**17a - Mixed-matrix membranes formed from imide-functionalized UiO-66-NH<sub>2</sub> for improved interfacial compatibility**

Qihui Qian (MIT)\*, Zach Smith (MIT)

Mixed-matrix membranes (MMMs) formed by dispersing metal-organic framework (MOF) particles in polymers have attracted significant attention because these composite systems can potentially surpass the separation performance of pure polymers alone. However, performance improvements are often unrealized because of poor interfacial compatibility between the MOF and the polymer, which results in interfacial defects. From a practical perspective, strategies are needed to address these defects so that MMMs can be deployed in real-world separation processes. From a fundamental perspective, strategies are needed to reliably form defect-free MMMs so that transport models can be applied to estimate pure-MOF property sets, thereby enabling the development of robust structure-property relationships. To address these interfacial challenges, we have developed a method to surface functionalize a UiO-66-NH<sub>2</sub> MOF with a nanoscopic shell of covalently tethered 6FDA-Durene oligomers. When combined with a high molecular weight 6FDA-Durene polymer of identical chemical structure to that of the imide-functional MOF surface, defect-free MMMs with uniform particle dispersions can be formed. With this technique, both permeabilities and selectivities of select gases in the MMMs were improved at loadings ranging from 5 wt% to 40 wt%. At a 40 wt% loading, CO<sub>2</sub> permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity were enhanced by 48% and 15%, respectively. Additionally, pure-MOF permeabilities for H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> were predicted from the Maxwell Model due to zero defects in the MMMs formed. Experiments have shown that this technique can be generalized to other MOF/polymer pairs, enabling the prediction of pure MOF transport property sets, which is impossible when defect-free pure-MOF membranes cannot be formed.

**TUESDAY 10:00 am** - Kings Garden 5

**17b - Janus polymers bearing tri(n-alkoxy)silyl side groups: glassy membrane materials with properties of rubbers**

Yury P Yampolskii (A.V.Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences)\*, Ludmila Starannikova (A.V.Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences), Dmitry Alentiev (A.V.Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences), Maxim Bermeshev (A.V.Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences), Eugene Finkelshtein (A.V.Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences)

A series of polymers of a new type, which contain rigid main chains (glassy nature) and flexible substituents (rubbery nature), were prepared from norbornene derivatives with Si(OR)<sub>3</sub>-groups where R= Me, Et, n-Pr, n-Bu. Two series of polymers, promising materials for membrane separation of gaseous hydrocarbons, were considered: metathesis and addition types substituted polytricyclononenes. The prepared addition polymers were glassy, while the glass transition temperature of metathesis polymers depended on the length of the alkyl-group R and varied in the range from -44 to 61°C. The dramatic tuning of polymer gas-transport properties was demonstrated by the change of the polymer main chain structure and the length of Si(OR)<sub>3</sub>-group. For example, we observed for the first time that obtained metathesis polymers turned out to be more permeable than their addition isomers. The novel polymers are not large free volume materials (Permeability coefficients P(O<sub>2</sub>) are in the range 16-190 Barrer), so they are devoid of common disadvantage of highly permeable polymers, fast aging and reduction of gas permeability. Meanwhile, all the studied metathesis and addition polytricyclononenes exhibited solubility controlled (or reverse) selectivity of permeation of hydrocarbons: ideal selectivity P(C<sub>4</sub>)/P(C<sub>1</sub>) for them was found to be in the range 13-49, higher than for many polymers with similar properties. The permeability coefficients of butane are also relatively great, up to 8100 Barrer. Doubtless, this new group of polymers can be considered as materials for membrane separation of hydrocarbons of natural and associated petroleum gases. \* This work was supported by Russian Science Foundation (grant #17-19-01595)

**TUESDAY 10:30 am** - Kings Garden 5

**17c - Solution processable metal organic frameworks for gas separations: from porous liquids to mixed matrix membranes**

Anastasiya V Bavykina (KAUST)\*, Alexander Knebel (Leibniz University Hannover Institute for Physical Chemistry and Electrochemistry), Shuvo Datta (KAUST), Magnus Rueping (KAUST), Mohamed Eddaoudi (KAUST), Juergen Caro (Leibniz University Hannover Institute for Physical Chemistry and Electrochemistry), Jorge Gascon (KAUST)

Conventionally the virtue of porosity is considered for porous solids, e.g. Metal Organic Frameworks (MOF), Porous Polymers or zeolites. Often their processability is not a focus of attention which hampers the application. We demonstrate that MOFs can be made solution processable via surface functionalization. We report on a solution processable ZIF-67. When placed in mesitylene, ZIF-67 predictably sediments. When it is modified and distributed within the same solvent, a clear solution formed with no sedimentation occurring for at least 24h. The morphology and textural properties of the modified MOF do not alter from the ones of its parent, which was confirmed by XRD, N<sub>2</sub> adsorption and SEM. Mesitylene has a kinetic diameter of 8.5Å and does not penetrate the pores, which are smaller in size. The system can be considered as a porous liquid - a novel class of porous materials. The modified MOF can either be directly employed as liquid membranes (LMs) or be co-processed with polymers to yield highly loaded mixed matrix membranes (MMMs). In a LM scenario, the permeation tests were carried out using a U-shaped permeation cell with equimolar C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> and CO<sub>2</sub>/CH<sub>4</sub> mixtures. While a pure solvent shows a separation factor for C<sub>3</sub>H<sub>8</sub>/C<sub>3</sub>H<sub>6</sub> mixtures close to 1, addition of the solid pore generator increases the separation. The permeance is higher than in solid membranes. The formation of dispersions of a MOF in a liquid is not limited by formation of porous liquids and application as LMs. We studied the advantages that this processability offers. Dispersions of functionalized ZIF-67 were blended with 6FDA-DAM in the shape of MMMs. While MMMs based on pure MOF maintain good physical resistance at low loadings, increasing the concentration of MOF results in brittle composites. In contrast, MMMs made from functionalized ZIF keep good mechanical strength even at ca. 50 wt.% loadings. The results obtained for this MMM are among the best MMMs ever reported for C<sub>3</sub>H<sub>8</sub>/C<sub>3</sub>H<sub>6</sub> separation.

**TUESDAY 11:00 am** - Kings Garden 5

**17d - Enhancing CO<sub>2</sub>/N<sub>2</sub> Selectivity and Elimination of Langmuir Sorption within High Tg, Glassy Polynorbornene Membranes**

Christopher Maroon (University of Tennessee), Jacob Townsend (University of Tennessee), Kevin Gmernicki (University of Tennessee), Daniel Harrigan (Aramco Services Company), Ben Sundell (Aramco Services Company), John Lawrence (Aramco), Shannon Mahurin (Oak Ridge National Laboratory), Konstantinos Vogiatzis (University of Tennessee), Brian Long (University of Tennessee)\*

We will describe how the CO<sub>2</sub>/N<sub>2</sub> gas separation performance of alkoxy-silyl-substituted vinyl-added polynorbornenes (VAPNBs) may be significantly enhanced via careful monomer design. More specifically, we will show that by increasing the incorporation of 5-tris(2-methoxyethoxy)silyl-2-norbornene in vinyl-added polynorbornenes, a substantial increase in CO<sub>2</sub>/N<sub>2</sub> selectivity may be realized with minimal decrease in CO<sub>2</sub> permeability. This trend avoids the traditional permeability/selectivity "tradeoff" relationship, and produces an optimal membrane whose performance nears the 2008 upper bound for CO<sub>2</sub>/N<sub>2</sub> separations. Though these polymers were initially designed to maximize CO<sub>2</sub> solubility, subsequent gas sorption studies revealed that these high Tg glassy membranes virtually lack any Langmuir sorption component, and indicate that their improved CO<sub>2</sub>/N<sub>2</sub> selectivity is due to decreased N<sub>2</sub> solubility within the matrix. This is further supported via computational modelling which suggests that the source of this apparent "N<sub>2</sub>-phobicity" is likely explained through comparative analyses of polymer-polymer and polymer-gas interactions. Finally, mixed-gas permeation tests were performed to provide a more realistic look at these membrane's real-world gas separation performance.

**TUESDAY 11:30 am** - Kings Garden 5

**17e - Ultra-High Permeability Mixed-Matrix Membranes as a Next-Generation Carbon Capture Technology for Post-Combustion**

Sameh K Elsaïdi (U.S. Department of Energy National Energy Technology Laboratory)\*, Surendar Venna (U.S. Department of Energy National Energy Technology Laboratory), Ali Sekizkardes (Battelle/U.S. Department of Energy National Energy and Technology Laboratory), Mona Mohamed (University of Pittsburgh), David Hopkinson (U.S. Department of Energy National Energy Technology Laboratory)

Mixed matrix membranes (MMMs) have great potential for separation applications including post-combustion carbon capture. To reduce the cost of capture and make them economically viable, new formulations with ultra-high permeability and moderate selectivity must be identified. Here, we present a bottom-up design of MMMs wherein the constituent materials have been designed for high gas separation performance and compatibility. MOF nanoparticles and polymers are decorated by desired functional groups that can chemically interact with each other to form defect free MMMs. The custom formulation of MMMs is important in scale-up production for practical applications. Successful formulation requires a blend of art and science. Here, two, three or four-components, were chosen for their compatibility, where each component has a different function and all are formulated with specific quantiles to fine-tune the physicochemical properties for defect free custom-formulated mixed-matrix membranes (CF-MMMs). PIM-1 and MEEP80 were combined with various MOF nanoparticles with different surface areas, pore sizes, and binding sites to conduct a parametric analysis of ten different membranes (CF-MMM-1 to CF-MMMs-10). The chemical interaction between the MOF nanoparticles and the polymer was the key facet for optimizing the interfacial compatibility between the polymer matrices and MOF fillers. Systematic variation of the compositions of these components and the type of MOF nanoparticles were performed to optimize the membrane separation performance affording enhanced CO<sub>2</sub> permeability (4200-25670 barrer) and CO<sub>2</sub>/N<sub>2</sub> selectivity (17-34) compared with the neat polymers. The permeability/selectivity values surpass Robeson upper bound and suggest the potential of these membranes for practical CO<sub>2</sub> separations. The scaling-up of these membranes were performed by preparing their components in a kilogram-scale, while their precise formulation allows technical feasibility of CF-MMMs fabrication.

**TUESDAY 12:00 pm** - Kings Garden 5

**17f - Composite gas separation membranes from metal-induced ordered polymeric frameworks**

Zhihua Qiao (Tianjin University), Song Zhao (Tianjin University), Menglong Sheng (Tianjin University), Jixiao Wang (Tianjin University), Zhi Wang (Tianjin University), Chongli Zhong (Tianjin University), Michael D Guiver (Tianjin University)\*

Metal-induced ordered microporous polymers (MMPs) are a new class of porous frameworks [1]. They are readily synthesized by polymer-directed chemical synthesis (PDCS) from functional polymers, small organic linkers and divalent metal ions. The small organic linkers coordinate with metal ions, and then the resulting unit cells self-assemble along the extension of the polymer chains, incorporating the polymer chains to construct three-dimensional frameworks as 50-100 nm nanoparticles. Variations in framework characteristics and pore sizes were achieved through choice of small organic linkers, metal ions, polymers and polymer molecular weight. Compared with conventional metal organic frameworks, MMPs show improvements in crystal size controllability and hydrolytic stability. MMP/mPSf membranes were fabricated by coating MMP dispersions onto modified polysulfone (mPSf) substrate, resulting in defect-free ultrathin gas-selective coated layers. Composite membrane MMP-3/mPSf had a CO<sub>2</sub> permeance of >3000 GPU and mixed gas CO<sub>2</sub>/N<sub>2</sub> (15/85) selectivity of 78, stable under both humid and dry gas feed conditions. MMP-1/PSf membrane had a CO<sub>2</sub> permeance of >5500 GPU and mixed gas CO<sub>2</sub>/N<sub>2</sub> selectivity of 35, placing them in the region of interest for CO<sub>2</sub> capture applications [2]. [1] Nature Materials 18 (2019) 163-168. [2] Journal of Membrane Science 359 (2010) 126-139.

**TUESDAY 2:00 pm** - Kings Garden 5

**18a - High temperature gas separation properties of sub-micron polybenzimidazole membranes**

Melanie M Merrick (The University of Texas at Austin)\*, Benny Freeman (The University of Texas at Austin)

Polybenzimidazoles (PBIs) are a class of polymer materials that have the potential to improve and expand the applications of commercial gas separation membranes. While many commercial membranes can only perform gas separations up to 100°C, PBIs are both chemically and thermally stable at temperatures up to 400°C. A potential application of PBI membranes is the high temperature hydrogen-hydrocarbon separations proposed by the NSF Engineering Research Center for Innovative and Strategic Transformation of Alkane Resources (CISTAR). Two novel aspects of this work are the previously unstudied ethane and ethylene gas separation properties at elevated temperatures and the temperature dependence of gas transport in sub-micron films over an expansive temperature range. Hydrocarbon gas separation properties of Celazole® PBI membranes were characterized at temperatures up to 190°C. Gas permeabilities, gas selectivities, activation energies of permeation, and physical aging rates differed significantly between thin sub-micron and bulk 20-micron Celazole® films. In particular, the activation energies of permeation were 1.5 to 4 times higher in an aged 450-nm thin film than in a 27-micron bulk film, suggesting a denser membrane structure and greater size-sieving ability. The first known evidence of physical aging in PBIs showed an 80 percent decrease in methane permeability over a 1000-hour period at 190°C for a 450-nm Celazole® film. This study elucidates the effects of elevated operating temperature on thin films by encompassing a broader and higher temperature range than previous studies of flat, sub-micron polymer membranes.

**TUESDAY 2:30 pm** - Kings Garden 5

**18b - Thermally Rearranged Semi-interpenetrating Polymer Network (TR-SIPN) Membranes for Olefin/Paraffin Separations**

Young Moo Lee (Hanyang University)\*, Won Hee Lee (Hanyang University), Jong Geun Seong (Hanyang University), Ho Hyun Wang (Hanyang University), Sun Ju Moon (Hanyang University)

Thermally rearranged (TR) polymers have received much attention in membrane gas separation applications due to their outstanding gas permeability [1]. Rigid chain structures constructed by TR processes can induce microporous morphology, resulting in improvement in gas transport characteristics [2]. Recent studies have aimed to use rigidity of TR polymers to enhance gas permeability by introducing cross-linkable agents [3] or preformed rigid moieties [4] into the TR polymer. In particular, TR polymers architected by network structures have been recently demonstrated to maximize rigidity and gas permeability [5]. Here, we report for the first time, TR-SIPN membranes composed of both linear and network TR polymers to attain polymer rigidity and to enhance olefin/paraffin separation performances. Facilely prepared TR-SIPN membranes exhibited noticeable rigid and microporous characteristics judging from BET surface area and gas sorption coefficients compared to conventional linear TR polymers. Moreover, the polymer matrices of TR-SIPNs, investigated by SAXS and gas permeation models, showed ideal structures in which large and small channels coexisted parallel to the gas transport direction. In olefin/paraffin separations, they retained more than 10 times higher gas permeabilities in ethylene and propylene gases without sacrifice in olefin/paraffin selectivities. As a result, they surpassed upper bound plots for ethylene/ethane and propylene/propane gas pairs. Furthermore, entirely rigid TR-SIPNs responded to outstanding plasticization resistances under aggressive pressures. References: [1] H.B. Park et al., *Science* 2007 318 (5848), 254-258; [2] M.D. Guiver and Y.M. Lee et al., *Science* 2013 339 (6117), 284-285; [3] M. Calle et al., *Macromolecule*, 2015 48 (8) 2603-2613; [4] Y.B. Zhuang J.G. Seong et al., *Macromolecules* 2015 48 (15), 5286-5299; [5] Y.S. Do and W.H. Lee et al., *Chem. Commun.*, 2016 52 (93) 13556-13559.

**TUESDAY 3:00 pm** - Kings Garden 5

**18c - Conformation-controlled molecular sieving effect for membrane-based propylene/propane separation**

Yang Liu (Georgia Institute of Technology)\*, William Koros (Georgia Institute of Technology), Mohamed Eddaoudi (KAUST), Gongping Liu (Georgia Institute of Technology), Youssef Belmabkhout (KAUST), Zhijie Chen (KAUST)

Membrane-based propylene/propane separation can reduce the operation cost in petroleum refining and petrochemical industries; however, identifying a suitable molecular sieve for membrane development is still challenging due to the close size ( $\sim 0.15\text{\AA}$  difference) between these two components. Our study addresses such a critical scientific question by a novel strategy. Specifically, with both C-C single bonds rotated (double eclipsed conformation), the C<sub>3</sub>H<sub>8</sub> molecule exhibits its minimum end-on essentially triangular shape but with a rotation energy barrier. Our strategy is to design/screen a "triangular" pore-aperture to allow only the double eclipsed C<sub>3</sub>H<sub>8</sub> conformer to pass through, effectively preventing all other C<sub>3</sub>H<sub>8</sub> conformers from diffusion jumps. This combination of factors leads to a very low C<sub>3</sub>H<sub>8</sub> diffusivity. On the other hand, the more compact C<sub>3</sub>H<sub>6</sub> molecule can pass through the pore-aperture with relative ease. According to our theoretical calculations based on transition state theory, a membrane with such desired pore-aperture can offer a C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> diffusion selectivity over a thousand. We further identified a MOF, Zr-fum-fcu-MOF, possessing the desired contracted triangular pore-aperture and fabricated mixed-matrix membranes using this MOF as an efficient filler. The fabricated hybrid membranes display very attractive C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> separation performance, far beyond the current trade-off limit of polymer membranes. Back-calculations using composite theory suggests the MOF displays a diffusion selectivity, like the ideally targeted, above 1000. This is the highest value reported for the C<sub>3</sub> pair to date, and we refer to this phenomenon as "conformation-controlled molecular sieving effect". Our work establishes a novel bottom-to-up strategy to develop membranes for gas separation and, meanwhile, refines the thinking on the molecular sieving effect to focus on the detailed geometrical characteristics comprising each gas molecule.

**TUESDAY 3:30 pm** - Kings Garden 5

**18d - Mixed matrix materials containing soluble discrete metal-organic polyhedra in rubbery polyethers for CO<sub>2</sub>/gas separation**

Haiqing Lin (The State University of New York at Buffalo)\*, Junyi Liu (The State University of New York at Buffalo), Cressa Fulong (The State University of New York at Buffalo), Tim Cook (The State University of New York at Buffalo)

Incorporating metal-organic frameworks (MOFs) in polymers is an effective strategy to improve membrane gas separation properties. For these mixed matrix materials (MMMs) to be fabricated into selective layers of 100 - 200 nm in industrial membranes, the MOFs particles should be smaller than 50 nm and have good compatibility with polymers to avoid defects at the interface of polymers and particles. In this work, soluble discrete metal-organic polyhedra (MOP) with particle sizes of  $\approx 5$  nm was synthesized and added into polyethers derived from poly(ethylene glycol) diacrylate (PEGDA) and poly(1,3 dioxolane) acrylate (PDXLA), which are leading materials for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub> separation. Interestingly, the introduction of the MOP-3 in the polyethers decreases glass transition temperature and even induces crystallization of polyPDXLA at higher loadings, indicating strong interactions between the polymer and particles. Increasing the MOP loading increases CO<sub>2</sub> permeability with a slight decrease in CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub> selectivity. For example, as the MOP content increases from 0 to 30 wt% in polyPDXLA, CO<sub>2</sub> permeability increases from 190 Barrers to 580 Barrers, and CO<sub>2</sub>/N<sub>2</sub> selectivity decreases from 70 to 62 at 35°C. These results can be satisfactorily modeled using the Lewis-Nielsen model with the MOP exhibiting much higher gas permeability than the polyethers. These MOP-based MMMs exhibit the separation properties above the Robeson's upper bounds for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub> separation. This talk will also compare these MMMs with those containing inherently insoluble ZIF-8 nanoparticles for the morphology and CO<sub>2</sub>/gas separation properties. Despite a body of studies of MMMs comprising MOFs, this work represents one of the few on the MMMs based on amorphous rubbery polymers elucidating the effect of soluble discrete MOP loading on the polymer properties and demonstrating their impact in achieving superior CO<sub>2</sub>/H<sub>2</sub> and CO<sub>2</sub>/N<sub>2</sub> separation properties

**TUESDAY 4:00 pm** - Kings Garden 5

**18e - Accessing novel microporous polymers to enhance yield, stereochemical control, and membrane performance in the recovery of light hydrocarbons from natural gas**

John Lawrence (Aramco Services Company)\*

Light hydrocarbons, i.e. propane and butane, provide additional value when recovered from natural gas due to their widespread use in energy and chemicals production. Current industrial approaches utilize energy-intensive refrigeration processes to recover light hydrocarbons, though the application of gas separation membranes can dramatically lower energy input and overall cost. Herein, we describe our efforts in developing novel microporous polymers to fabricate membranes capable of selectively removing light hydrocarbons from natural gas streams. Utilization of a new synthetic pathway enabled the synthesis of stereochemically pure monomers bearing bulky, rigid substituents with varying connectivity to the polymer backbone in order to study how increasing polymer rigidity through pendant group chemistry affects polymer synthesis, chain packing, and membrane performance. Immediate benefits of the enhanced stereochemical control gained using this synthetic pathway were evident in the polymerizations, where the one polymerization route proceeded in yields up to 100%. NMR analysis confirmed monomer and polymer structure, while XRD revealed increased interchain spacing when bulky pendant groups are present. More importantly, single and mixed gas permeation studies demonstrated a dramatic increase in  $C_4 H_{10}$  permeability and  $C_4 H_{10}/CH_4$  selectivity when pendant group structure and connectivity were optimized. For example, at 800 psi in mixed gas feeds, increased cyclic content in one of the polymer structures improved  $C_4 H_{10}$  permeability from 321 Barrer to 739 Barrer and  $C_4 H_{10}/CH_4$  selectivity from 9.8 to 12.8 when compared to the analogous polymer lacking this connectivity. Even more interesting, changing the substituent off the pendant group had a profound effect on permeation properties and further enhanced performance, achieving a  $C_4 H_{10}$  permeability of 6520 Barrer and  $C_4 H_{10}/CH_4$  selectivity of 19.6.

**TUESDAY 4:30 pm** - Kings Garden 5

**18f - Insight into the transport in polymeric and mixed matrix membranes via analysis of unique mixed gas diffusion coefficients**

Johannes Carolus (John) Jansen (National Research Council of Italy)\*, Alessio Fuoco (National Research Council of Italy), Marcello Monteleone (National Research Council of Italy), Elisa Esposito (National Research Council of Italy)

Gas separation by polymer membranes is an expanding technology in many application fields, such as oxygen or nitrogen separation from air (i.e. separation  $O_2/N_2$ ) or biogas upgrading [1] and natural gas treatment (i.e. separation  $CO_2/CH_4$ ), and others. Over the years, many new polymers have been developed, and their performance is typically expressed in terms of their position in the Robeson diagram [2,3]. Improvement of the performance requires a rational design of the polymer [4] and detailed knowledge of the transport properties. For a better understanding of the membrane performance, studies must not be limited to the more common single gas permeability alone, but they should be extended to gas mixtures and to diffusion as well as solubility. In this work we discuss a novel method that uses on-line mass spectrometric analysis of the permeate composition during the transient phase, enabling the unique determination of mixed gas diffusion coefficients, besides permeability coefficients [5,6]. Using some typical examples, we will discuss the difference between pure and mixed gas permeation and diffusion in standard membranes, the effect of porous fillers in mixed matrix membranes, and the effect of the gas-membrane affinity in membranes with anomalous transport. For instance, we will show how a MOF in low free volume polymers decreases the apparent diffusion coefficient via its increased sorption capacity, while functional groups in high free volumes effectively decrease the diffusion coefficient and promote selectivity by competitive sorption. [1] E. Esposito, J.C. Jansen et al., *Energy Environ. Sci.* 2019, 12, 281-289. [2] L.M. Robeson, *The upper bound revisited*, *J. Membr. Sci.*, 2008, 320, 390-400. [3] R. Swaidan et al., *ACS Macro Lett.*, 2015, 4, 947-951. [4] B. D. Freeman, *Macromolecules*, 1999, 32, 375. [5] S.C. Fraga, J.C. Jansen et al., *J. Membr. Sci.*, 2018, 561, 39-58. [6] M. Monteleone, J.C. Jansen et al., *Membranes*, 2018, 8, 73.

**TUESDAY 2:00 pm** - Kings Garden 4

**19a - Minimizing the cost of membrane distillation**

Timothy V Bartholomew (Carnegie Mellon University)\*, Alexander V Dudchenko (Carnegie Mellon University), Nicholas Siefert (U.S. Department of Energy National Energy Technology Laboratory), Meagan S Mauter (Carnegie Mellon University)

This work presents a modeling platform for assessing the energy consumption and cost of membrane distillation (MD). We leverage multi-objective nonlinear programming models to maximize the gained output ratio (GOR) and minimize the levelized cost of water (LCOW) of membrane distillation for multiple module designs (i.e. direct contact, air gap, conductive gap, sweeping gas, and vacuum) and system configurations (i.e. single or multi-stage, pass through or looping). This optimization approach identifies the energy or cost optimal design and operation for a specified water recovery, feed salinity and flowrate, and process and financial parameters. Our system-scale model includes a detailed finite difference module-scale model that explicitly considers the pressure drop along the module and non-constant solution properties (i.e. density, diffusivity, non-ideality, specific heat) and mass and heat transfer coefficients. We explore the influence of parameter uncertainty inherent in emerging technologies by simulating process performance across a range of parameter values to develop distributions for the expected GOR and LCOW and identify generalizable guidelines for energy efficient and low-cost membrane distillation.

**TUESDAY 2:30 pm** - Kings Garden 4

**19b - Process Optimization Using Perturbation Expansion Solutions for Membrane Gas Separation Modules**

Norfamila Che Mat (Universiti Malaysia Sarawak ), Glenn Lipscomb (University of Toledo, Toledo)\*

Simulation and optimization of hybrid membrane gas separation processes, such as those proposed for carbon capture, require high fidelity module performance simulations. Unfortunately, these simulations require iterative solution techniques which can be sensitive to the initial solution guess and thus require extensive iteration (i.e., computational time) or fail to converge. Perturbation solutions to the isothermal, constant transport property, multi-component cross-flow and counter-current flow performance equations are presented. Predictions from the direct, non-iterative solution are compared to solutions obtained using numerical approximations. Excellent agreement is found in all cases even for systems with broad ranges of recovery for feed gas components. The results also are excellent initial guesses for simulations that account for module non-idealities. The use of these solutions in optimizing staged membrane systems is discussed. The perturbation solution can dramatically speed up optimization and help identify unfeasible configurations.

**TUESDAY 3:00 pm** - Kings Garden 4

**19c - Multi-physics Simulation of Hollow Fiber Vacuum Membrane Distillation Using OpenFoam**

Albert Kim (University of Hawaii)\*, Ho Ji (Korea Research Institute Of Ships And Ocean Engineering), Deok-Soo Moon (Korea Research Institute Of Ships And Ocean Engineering), Hyeon-Ju Kim (Korea Research Institute Of Ships And Ocean Engineering)

A VMD module often consists of three regions of feed solution, low-pressure gas, and porous membrane. At interfaces of the regions, at least two transfer phenomena are coupled. On the feed-membrane interface, liquid feed evaporates, and vapor molecules migrate through void spaces of the porous membrane. Momentum and heat transfer in the liquid feed can be described using coupled Navier-Stokes and Fourier equations. Migration of vapor molecules and heat transfer is at the level of molecular kinetic motion through the membrane pores, where molecular convection and diffusion are dominant. In the (low-quality) vacuum phase of the distillate, it is questionable to apply continuum-based flow models or rarefied gas models. Overall, modeling studies on VMD are fundamentally challenging because the phenomena are not only intrinsically coupled for transports, but also of multi-scales at the molecule, pore, and module levels. In industrial applications, a VMD module has a large number of fibers of an order of a few hundred or thousand. As each hollow fiber is treated as a mass source of vapor distillate, a continuum model for packed hollow fibers is fundamentally of flaw to predict the VMD performance. In this vein, the current paper investigates the VMD module of realistic sizes, containing hollow fibers of an order of 100, and simulate the coupled transport of momentum, heat, and mass in a seamlessly combined manner. For this study, OpenFOAM (an open-source CFD package) is used to solve for the thermal flow of liquid water and vapor molecules. We used a theoretical interpretation to enhance the computational efficiency and modified OpenFOAM solvers to rigorously investigate the multi-physics, multi-scale phenomena. Computational techniques and physical interpretations will be discussed in detail.

**TUESDAY 3:30 pm** - Kings Garden 4

**19d - Scale-up of Facilitated Transport Membrane Module for CO<sub>2</sub> Capture from Flue Gas**

Kai Chen (Ohio State University)\*, Witopo Salim (Ohio State University), Yang Han (Ohio State University), Dongzhu Wu (Ohio State University), Winston Ho (Ohio State University)

In order to modularize a composite membrane with an ultrathin selective layer, it is a challenge to scale up the membrane fabrication procedure from lab to pilot scale. Herein, a knife-coating method was successfully integrated into a roll-to-roll fabrication machine, making a 165-nm thick facilitated transport membrane for CO<sub>2</sub> capture from flue gas with 14 inches in width and > 1200 feet in total length. The scale-up membranes were subsequently used to make spiral-wound (SW) elements and modules. To increase the membrane packing density in a single element, a detailed multi-leaf rolling procedure was developed to scale up the elements efficiently. Although the fabrication of a multi-leaf SW membrane module has been well recorded in the literature, the majority of the methods had all the membrane leaves directly attached to the central permeate tube, thus, the number of leaves was limited by the central tube surface area. In order to improve the fabrication, the glue lines were modified to allow an arrangement of a stack of staggered membrane leaves not attached to the central tube before rolling. Moreover, the spacer thickness was reduced to as low as 6 mil, which further increased the membrane area to 2.94 m<sup>2</sup> in the most recent modules. The modules also reproduced the transport performance of the flat-sheet membrane under various testing conditions. For instance, a CO<sub>2</sub> permeance of 1450 GPU and a CO<sub>2</sub>/N<sub>2</sub> selectivity of 185 were showed with a simulated flue gas at 67°C. In addition, satisfactory pressure drops were also achieved. From the first successful SW element made in house to the most recent ones, a scale-up factor of >70 was achieved. A predictive model was developed to relate the operating conditions to the module separation performance, accounting for the limitations set by concentration polarization and pressure drop. The experience gained is helpful to design a full-sized element (40 inches in length and 8 inches in diameter) for industrial application.

**TUESDAY 4:00 pm** - Kings Garden 4

**19e - Development of industrial scale polyvinylidene fluoride transfer membrane**

Marta E Bojarska (GVS Filter Technology)\*, Deb English (GVS Filter Technology), Gil Tavares (GVS Filter Technology)

One of many life science applications is blotting, which is a method of proteins, DNA or RNA transferring onto a polymeric material that is called a transfer membrane. Typically transfer membranes are manufactured from polyvinylidene fluoride (PVDF), nitrocellulose (NC) or Nylon (NY). In techniques such as Western Blotting or Dot Blot, which are used for protein transfer, mainly PVDF and NC membranes are used. Transfer of proteins onto the membranes mostly depends on material ability to bind the proteins. The binding might be based on a hydrophobic or electrostatic interaction between the membrane and the protein. Present work will mainly focus on the development of polyvinylidene fluoride membrane for protein transfer. Hydrophobic PVDF membrane can be manufactured via Non-solvent Induced Phase Separation (NIPS), where the cast film of polymeric solution (PVDF + solvent + additives (optional)) is immersed into the coagulation bath (non-solvent or mixture of solvent and non-solvent). This technique, depending on the process parameters, allow obtaining both asymmetric and symmetric membranes. One also need to have in mind that factors such as grade of polyvinylidene fluoride, solvent type, as well as process parameters of dope solution preparation, casting and coagulation can influence membrane surface characteristic and its affinity towards proteins. In this work, the main focus will be put into subtle differences between the membranes morphology and surface characteristic that allows obtaining better sensitivity during Western Blotting or Dot Blot. At the same time, standard membrane characterizations such as air flow rate, water breakthrough, capillary flow porometry, SEM, contact angle, and protein binding were performed. Present work provides an insight into an industrial membrane manufacturing with a scientific touch for details in reference to life science applications.

**TUESDAY 4:30 pm** - Kings Garden 4

**19f - Low energy seawater desalination using multistage electro dialysis**

Gijs Doornbusch (Eindhoven University of Technology)\*, Michele Tedesco (Wetsus), Jan Post (Wetsus), Zandrie Borneman (Eindhoven University of Technology), Kitty Nijmeijer (Eindhoven University of Technology)

Due to the economic and population growth, unavoidable problems arise, such as fresh water scarcity. Electrodialysis (ED) is a well-established electrochemical desalination technology based on ion exchange membranes. In an ED system, ions migrate through anion and cation selective membranes due to the applied stack potential. Energy consumption of the system strongly depends on the salt concentration of the feed solution. Due to the high operational costs compared to seawater reverse osmosis (RO), ED is currently not used for seawater desalination. Although RO is the state-of-the-art seawater desalination technology, due to technological limitations further reduction of energy consumption (2 kWh/m<sup>3</sup>) is not apparent. A strong benefit of ED compared to RO not seriously considered so far, is the possibility of staging of different ED stages. In such an approach each ED stack is operated at its optimum conditions (different current densities) aligned with the governing feed water conditions at that stage, unlike in the case of single-stage operation. This research shows the potential of staging in ED as an effective approach for seawater desalination. We experimentally compared single-stage ED with multistage ED (four desalination stages) and investigated the effect of operational parameters for both systems. Different current regimes show that multistaging in ED can be an effective tool to desalinate seawater. Using one single stage with the same membrane and electrode area as the four stages of the multistage does not allow for full desalination. Oppositely, drinking water can be produced in the multistage when operating each stage close to 95% of the measured limiting current density. The lowest energy consumption obtained while reaching the lowest diluate concentration is 3.6 kWh/m<sup>3</sup>, confirming that ED can be considered as an energy-effective desalination technology, potentially able to desalinate seawater at a competitive energy consumption compared to RO.

**TUESDAY 2:00 pm** - Kings Garden 3

**20a - Air Products Hybrid Membrane Adsorption**

Cory E Sanderson (Air Products and Chemicals)\*, Don Henry (Air Products and Chemicals)

Light noble gases, primarily Helium and Neon, are rare in Earth's atmosphere and upper mantle and difficult to produce. Yet the gases are highly valuable to the many diverse markets which depend on their specific chemical and physical properties. Air Products has developed a hybrid membrane and adsorption process to extract and purify a light noble gas from a feed gas stream which has low and variable concentrations of the light noble gas at both high recovery and low unit cost. The process combines the best features of both unit operations- high light noble gas selectivity compared to bulk gases of Methane and/or Nitrogen, with a unique recycle control loop to create a process which has superior performance over any membrane or adsorption only process. The process has flexibility in both scale and source of gas which gives it a wide application and potential implementation strategy.

**TUESDAY 2:30 pm** - Kings Garden 3

**20b - Hybrid Distillation and Facilitated Transport Membrane Processes for C3 Splitter Debottlenecking**

Kenneth Pennisi (Compact Membrane Systems), Christine Parrish (Compact Membrane Systems)\*, Sudip Majumdar (Compact Membrane Systems)

Propylene and propane are very important hydrocarbons in the global economy. Propylene is used to manufacture polypropylene, a very widely used polymer, as well a variety of important chemicals such as, acrylonitrile, propylene oxide, cumene, acrylic acid, and isopropanol. Propane is a widely used fuel. Obtaining these two hydrocarbons in sufficient purity for end uses almost always involves distillation to separate them from each other. Due to their low relative volatility, the distillations columns have many trays and operate at high reflux ratios. Consequently, capital and energy costs of the separation are high. Many propylene producers have been forced to operate their distillation columns at maximum capacity in an effort to keep up with rising demand. Since demand generally continues increasing year over year, many producers currently have a need for a means to meet incremental demand increases that is not as capital intensive as replacement of the distillation column. Compact Membrane Systems, Inc. has developed a novel membrane technology which can efficiently separate propylene and propane, as well as other olefin/paraffin mixtures. When retrofitted to an existing distillation column, the membrane can debottleneck the separation step of the production process. Furthermore, economic analysis has shown the approach to be very cost effective. In this paper, we will examine some of the options for configuration of the retrofit and evaluate the process economics of each.

**TUESDAY 3:00 pm** - Kings Garden 3

**20c - Water Recovery via Forward Osmosis - Freeze Concentration**

Georgios Kolliopoulos (University of Toronto), Jeffrey Martin (University of Toronto), Chenbo Xu (University of Toronto), Vladimiro Papangelakis (University of Toronto)\*

Contaminants accumulate in industrial process circuits before their disposal in tailings ponds. The unstable nature of the latter often leads to catastrophic accidents such as acid mine drainage and is a threat to the prosperous development of the local communities as well as a liability for industry and governments. Therefore, energy efficient water recovery technologies are of critical importance, especially in today's era of increased environmental awareness. Recently, at the University of Toronto, we developed a proprietary green technology system to recover water from such contaminated aqueous streams. Our technology is a climate-driven hybrid forward osmosis - freeze concentration, which relies on two-steps to achieve fresh water recovery. First, water spontaneously permeates from multi-component effluents into environmentally benign single-solute inorganic draw solutions with no external energy input via forward osmosis. The above is the result of the osmotic pressure gradient between a dilute feed solution (i.e., the effluent) and a more concentrated solution (i.e., the draw solution). Subsequently, the resulting inorganic diluted solution is exposed to a temperature below its freezing point to recover water as ice, while regenerating the draw solution. Water recovery by freezing is similar to distillation but is 7 times more energy efficient. The cold winter climate in northern territories, where many industrial activities (e.g., mining) took place, operate, or are scheduled to be in operation in the next few years, can be leveraged to produce fresh water and decontaminate the land upon stabilizing the aqueous wastes via forward osmosis - freeze concentration. Hereby, we report on experimental forward osmosis and freeze concentration results for a series of inorganic draw solutions, the estimated required energy to drive our technology system, as well as a comparison of our technology with industry standards.

**TUESDAY 3:30 pm** - Kings Garden 3

**20d - Leverage membrane technology in process intensification and new application design - from early stage design to technical scale implementation**

Peter Kreis (Evonik Technology & Infrastructure GmbH)\*, Kah Peng Lee (Evonik Fibres GmbH), Lars Peters (Evonik Fibres GmbH), Erik Hoving (Evonik Cooperation), Steven Pedersen (Evonik Canada Inc.), Kumar Abhinava (Evonik Cooperation)

For many separation process applications, conventional technologies like distillation, extraction and absorption are still the first choice in a conceptual separation design. New separation technologies such as membrane or membrane based hybrid separations are often not considered although advanced membrane materials and simulation infrastructure has significantly developed in recent years. Step-changes in process intensification and product-by-process applications are possible, if these technologies are considered at early stage. Beyond their stand-alone operation, membrane units are particularly effective when combined with established, often thermal, separation processes in an intelligent configuration. In this way, membrane processes have maximum impact and exhibit their advantage in synergy with other basic unit operations, while the limitations of a stand-alone membrane process are mitigated. For example, early stage design with organic solvent nanofiltration have led to new industrial efficient and low energy consuming applications in homogeneous catalyst recovery but also in the recovery of THC and CBD from cannabis. Another emerging field of using membranes over classical separation processes is upgrading of biogas to renewable natural gas and in the field of natural gas sweetening. In this talk, we give an overview about the application diversity of membranes. We show why it is critical to consider membrane processes early on during the conceptual design process and how membrane technology leads to success.

**TUESDAY 4:00 pm** - Kings Garden 3

**20e - Carbon Capture utilizing Hybrid Membrane/Liquifaction**

David Hasse (Air Liquide)\*

Air Liquide has developed multiple hybrid CO<sub>2</sub> capture processes based on hollow-fiber membrane operation in combination with cryogenic distillation. (ref 1, 2, 3) Membranes offer unique ability to achieve high recovery, while distillation allows unrivalled purity. CO<sub>2</sub> purification is limited by the triple point of CO<sub>2</sub>. If it was not for this thermodynamic barrier, large scale distillation similar to air separations would be the preferred method for CO<sub>2</sub> capture at large scales. However, CO<sub>2</sub> liquifaction is limited to low recovery at low concentrations unless uneconomically large pressures are used. Membranes offer a solution to raise the recovery while maintaining purity. Three separation techniques will be discussed. CO<sub>2</sub> capture from air fired coal, where the CO<sub>2</sub> is at low concentration, CO<sub>2</sub> capture from oxy-fired coal, where the CO<sub>2</sub> is at high concentration, and CO<sub>2</sub> capture internal to an SMR, where the diluent gas is hydrogen. Each case provides unique issues, and a hybrid membrane solution is an optimal solution. This is a true hybridization, with a recycle loop between processes. References: Energy Procedia Hasse et al, volume 63, pages 186-193 (2014) Energy Procedia Lockwood et al, volume 63, pages 342-351 (2014) Energy Procedia Pichot et al, volume 114, pages 2682-2689 (2017)

**TUESDAY 4:30 pm** - Kings Garden 3

**20f - Membrane distillation hybridized with a thermoelectric heat pump for energy-efficient water treatment and space cooling**

Yong Zen Tan (Nanyang Technological University), Nick Guan Ping Chew (Nanyang Technological University), Wai Hoong Chow (Nanyang Technological University), Rong Wang (Nanyang Technological University), Jia Wei Chew (Nanyang Technological University)\*

The current concept for cooling the indoors is far from ideal with respect to the total energy consumed and waste discharged. A novel concept for improving the energy efficiency is proposed via hybridizing the heat pump with a membrane distillation (MD) unit for simultaneous space cooling and water treatment. MD is well-acknowledged for utilizing low-quality waste heat for water treatment, which makes it feasible for coupling with a heat pump to make use of both the hot and cold reservoirs of the pump. Accordingly, the objective of the current effort was to investigate via experiments the efficacy of a thermoelectric heat pump coupled with a sweep-gas MD system (T-SGMD) by measuring the cooling capacity, condensate production and power consumption. The results from this study can be extended to other heat pumps. Three key highlights emanated from this study. Firstly, condensate production per unit energy consumed can be doubled with the T-SGMD system relative to thermoelectric dehumidification alone. Secondly, cool air recycle affected the condensate flux the most without a drastic loss of cooling compared to other tested parameters during the operation of the T-SGMD. Lastly, the T-SGMD system was able to provide an increase in condensate produced per unit energy without a loss in cooling capacity per unit energy input. These advantages of coupling heat pumps with MD, leveraging on the current advancements in MD, is promising for a hybridized system for decentralized water treatment, dehumidification and space cooling.

**TUESDAY 2:00 pm** - Ballroom 3

**21a - Reduction of Brackish Water Desalination Brine Volume using Membrane Evaporation Coupled with Activated Sludge Aeration Waste Heat**

Drew W Johnson (The University of Texas at San Antonio)\*

Desalination processes produce highly concentrated brine effluent which is costly to dispose of for inland brackish water desalination facilities. The current study focuses on membrane evaporation processes to reduce brine disposal volume where brine concentrate is a cold fluid that enters inside hollow fiber lumens while exposing the outer surface to low grade heat obtained from compressed air at wastewater treatment facilities. Aeration is the most energy-intensive operation in wastewater treatment, amounting to 45-75% of plant energy costs. During aeration, the compression of the air causes an increase in air temperature (often modeled as adiabatic). This waste heat can be utilized to drive heat and mass transfer operations for evaporating brine concentrate from inside the membrane. As an example, the activated sludge water recycling center for the city of San Antonio TX treats 303 MLD of wastewater in a two-stage aeration mode by providing 1,400 MLD of air with a rated discharge pressure of 186 kPa and a temperature of 345 K. For these conditions, membrane evaporation was evaluated at the bench scale for a brackish water brine at different brine flow rates, airflow rates and air temperatures, extent of fouling and possible means to control fouling. The evaporation rate was found to increase with airflow rate and air temperature and decrease with brine flow rate. Model predictions, derived based upon literature values for heat and mass transfer correlations, agreed well with the measured evaporation rates. Fouling was observed in experiments for brine with and without ferrous iron. Cleaning of the membranes by flushing the fibers with brine at higher flow rates was not able to alleviate fouling. Fouling could be alleviated when the pH of the brine solution was lowered for the duration of the studies conducted. The economics of the proposed process appear favorable if energy demands are neglected when using waste heat.

**TUESDAY 2:30 pm** - Ballroom 3

**21b - Smart High Recovery RO Boosts Recovery Rate to More Than 90% for Reuse Purposes**

Ronit Erlitzki (AdEdge Water Technologies)\*

Concentrate management is a key issue for the use of reverse osmosis (RO) technology. Reducing the amount of RO concentrate is critical for all inland RO applications. This paper will present a case history of a reverse-osmosis plant located in Southeast Asia that is using municipal treated tertiary effluent for industrial reuse purposes. The recovery rate (RR) of the system was limited to 75% due to scaling from relatively high feed water concentrations of phosphate, calcium, and iron, resulting in frequent CIP cycles. Attempts to increase RR by conventional methods to 85%, led to increase in CIP frequency from 1 - 3 months to about two weeks. To improve the performance in a cost-effective manner, the existing 2,000 gpm RO was retrofitted in early 2017 with Flow-Reversal (FR) technology. Currently, the retrofitted train is operating at 90% RR with the same CIP interval that was required to achieve the lower RR. The RR is expected to increase gradually to achieve higher than 90% while keeping the balance between RO recovery, CIP intervals, and water production optimization. The increase in water production has translated into 60% decrease in concentrate volume, a 20% growth in annual revenue, and a return on investment of 1.5 years. The Flow-Reversal RO technology employs conventional RO equipment with two unique functions to improve recovery. The first is allowing each array of RO vessels to periodically function as the third stage in the process. The second, which happens concurrently, is periodically reversing the direction of the feed stream through each one of the pressure vessels. This approach reduces the adverse effects of scaling by rotating to the next group of pressure vessels before scale is precipitated out, and by switching the direction of feed stream to flush out what small amount of scale that might have embedded on the membrane surface.

**TUESDAY 3:00 pm** - Ballroom 3

**21c - Membrane Distillation for Enhanced Water Recovery by Inland Brackish Water Desalination Plants**

Zhewei Zhang (University of Pittsburgh)\*, Radisav Vidic (University of Pittsburgh)

Inland brackish water (BW) desalination plants typically use reverse osmosis (RO) for the production of drinking water. However, low water recovery (i.e., 50 - 75%) results in fairly large quantities of the reject (concentrate) stream that needs to be disposed at considerable cost and potentially significant adverse environmental impacts. Membrane distillation (MD) offers a unique opportunity to improve the performance of these BWRO plants by recovering additional clean permeate from the reject stream, thereby reducing the volume of concentrate that needs disposal. Unlike RO that uses pressure to drive water through the membrane, MD relies on the vapor pressures difference between the feed and permeate to reject all inorganic and non-volatile organic contaminants and recover almost pure water on the permeate side. Membrane fouling and wetting due to precipitation of common salts on the feed side (e.g., gypsum, silica) affect MD performance in terms of flux decline and deterioration in permeate quality. Therefore, appropriate feed pretreatment to remove potential scaling components and ensure high water recovery from the reject stream is essential for the application of this treatment technology. In this study, barite precipitation was utilized to remove sulfate from actual BWRO concentrate as the key precipitate that would interfere with MD operation. The effect of barium concentration and mixing condition was evaluated for its impact on the removal of sulfate and silica as the most common inorganic scales. The pre-treated BWRO concentrate was treated in direct contact membrane distillation (DCMD) system to achieve at least 80% water recovery. The performance of optimized pretreatment process and DCMD design and operating parameters will be discussed together with the impact of MD treatment on the overall performance of inland desalination plants in terms of water recovery and environmental impacts.

**TUESDAY 3:30 pm** - Ballroom 3

**21d - Selective Separation of Industrial Relevant Metal Ions from High TDS Water using Wafer-Enhanced Electrodeionization (WE-EDI)**

Humeyra B Ulusoy Erol (University of Arkansas)\*, Christa Hestekin (University of Arkansas), Jamie Hestekin (University of Arkansas)

There is a need for an efficient and economical process of ion-selective separation. In hydraulic fracturing, for instance, several million gallons of water are used in a site, most of which are disposed of by deep well injection taking the water from the ecosystem and causing earthquakes. However, due to the high amount of ions in wells at fracking sites, pressure driven processes for water recovery are impossible to use. This project will demonstrate an emerging environmentally friendly Wafer Enhanced Electrodeionization (WE-EDI) technology which attempts to eliminate the shortcomings that come with normal EDI and separates effluent streams into concentrated ions and clean water. In WE-EDI, ion-exchange resins are replaced by wafers that consist of cation and anion exchange beads and a polymer binding agent. In this study, selective separation of these ion exchange wafers and the effect of electroosmotic drag on the membrane structure have been performed for various anions and cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>) and improved selectivity and higher water recoveries have been observed while significant modeling has taken place to predict the selective separation as a strong function of the equilibrium constants between the ions and the beads.

**TUESDAY 4:00 pm** - Ballroom 3

**21e - Pilot Evaluation of Closed Circuit Reverse Osmosis (CCRO) for Treatment of RO Concentrate for Potable Reuse**

Han Gu (Orange County Water District)\*, Megan Plumlee (Orange County Water District), Mike Boyd (Desalitech), Ran Nadav (Desalitech), Michael Hwang (Jacobs), Jim Lozier (Jacobs)

The Orange County Water District (OCWD) Groundwater Replenishment System (GWRS) purifies secondary wastewater for potable reuse and currently discharges 18 million gallons per day (MGD) of RO concentrate (ROC) to the ocean. This will increase to ~23 MGD after plant expansion in 2023. OCWD seeks to identify a cost-effective approach to minimize RO concentrate waste and generate new water supply for the region. A field pilot evaluation of Desalitech's Closed Circuit Reverse Osmosis (CCRO) technology was conducted at OCWD to recover water from ROC. CCRO recirculates its concentrate until the desired recovery is reached. The objective of the test was to evaluate the performance of CCRO technology in terms of recovery, clean-in-place (CIP) frequency and permeate quality. This presentation will focus on challenges experienced (organic fouling, mineral scaling, and ROC water quality fluctuations) and adaptive control strategies that improved performance at GWRS. When CCRO was operated with GWRS ROC as the feed, rapid permeability decline was observed and suspected to be caused by organic fouling based on membrane autopsy. Treating ROC while using GWRS RO feed (i.e., microfiltration effluent) to refill the CCRO side conduit at the end of each cycle extended run time by more than two fold. In addition, high cross flow velocity was shown to improve mixing and reduce fouling. ROC water quality fluctuations also created a major challenge for maintaining performance. To address these fluctuations in feed water quality, the maximum recovery, concentrate conductivity, and feed pressure were used as thresholds to engage the end/re-start of each cycle. Instead of running at a preset maximum recovery, the pilot is operated in a variable recovery mode where the cycle-to-cycle recovery is controlled by both the maximum concentrate conductivity and recovery setpoint. Two long-term, continuous runs were successfully completed to confirm the optimal CIP frequency of the CCRO pilot.

**TUESDAY 4:30 pm** - Ballroom 3

**21f - Brine Treatment for Minimal and ZLD**

Malynda Cappelle (The University of Texas at El Paso)\*, W. Shane Walker (The University of Texas at El Paso)

Globally, demand for water and energy are increasing with increasing population. High recovery desalination can mitigate environmental and economic concerns with brackish desalination by minimizing the amount of liquid waste. Zero Discharge Desalination (ZDD) has been demonstrated to achieve up to 98% recovery from brackish water while producing suitable water for drinking water, industrial, or agricultural purposes. ZDD combines a pressure-driven desalination process (reverse osmosis or nanofiltration) to produce high quality drinking and irrigation water and an electrically-driven process (electrodialysis metathesis) to reduce concentrate volume and improve system recovery. A study was performed using a mathematical ZDD model, which was expanded to include byproduct recovery, specifically sodium chloride (which is used for the EDM process in ZDD), as well as calcium sulfate and magnesium hydroxide. The updated ZDD model was used to evaluate the economic tradeoffs in ZDD design. The model results indicate that for a fixed water chemistry, the unit cost of water 1) decreases with decreasing salt rejection of the primary desalting membrane, 2) decreases with increasing RO/NF recovery, and 3) decreases with decreasing EDM membrane resistance. A sensitivity analysis was performed for a ZDD design with NF operating at 75% recovery (hybrid NF90-NF270 staging), and the results of this analysis suggest that the unit cost 1) increases by 13-18% if more efficient, more expensive EDM membranes are employed, 2) is substantially affected by EDM equipment and power unit cost assumptions, and 3) is only slightly impacted by RO/NF equipment and evaporation pond cost assumptions; however the membrane choice and RO/NF recovery do have a noticeable impact on product water quality, ZDD specific energy consumption, and ZDD system recovery. The incorporation of salt recovery decreased the cost of all ZDD designs by approximately 10-30%, even when revenue from salt sales was excluded.

**TUESDAY 2:00 pm** - Ballroom 4

**22a - Novel Spirocyclic Polymers for Membrane-based Organic Solvent Separations**

Ronita Mathias (Georgia Institute of Technology)\*, Kirstie Thompson (Georgia Institute of Technology), Dhaval Bhandari (Exxon Mobil), JR Johnson (Exxon Mobil), Huaxing Zhou (Exxon Mobil), M.G. Finn (Georgia Institute of Technology), Ryan Lively (Georgia Institute of Technology)

Solution-processable microporous polymers have the potential to outperform traditional polymeric membranes in the area of organic solvent separations. In this work, novel spirocyclic polymers were incorporated into thin-film composite membranes with the aim of improving solute rejection when compared against current spirocyclic polymers such as PIM-1. The separation system of interest is a complex mixture of hydrocarbon solvents that are typically found in the light fractions of crude oil. These compounds were utilized not only to create a molecular weight cut-off (MWCO) curve but also to assess the performance of this class of membranes in the fractionation (as opposed to purification) of complex mixtures. We find that the novel spirocyclic polymers have higher rejections than PIM-1 membranes, although the permeances are lower using our non-optimized thin film composite fabrication techniques. A MWCO of ~ 250 Da can be obtained, which is accompanied by high selectivities amongst different classes of hydrocarbons of a similar size. Moreover, high selectivities are also observed amongst molecules within the same class with only a sub-nm difference in size. Such size- and shape-selective separation enables the use of these polymeric membranes in a wide range of applications.

**TUESDAY 2:30 pm** - Ballroom 4

**22b - 3D Printed fouling resistant composite membranes**

Davide Mattia (University of Bath)\*

The formation and growth of fouling layers is a long-standing challenge for the continuous operation of membrane processes. Membrane patterning is considered as a potential route for fouling mitigation by promoting shear stress and creating localised turbulence near the membrane surface. Patterned membranes have been fabricated using a variety of techniques, e.g., moulding and stamping, which lack sufficient fidelity and flexibility, limiting their actual use. 3D printing allows overcoming these challenges by enabling the design and fabrication of complex patterns impossible to manufacture otherwise.<sup>1</sup> In this paper we report the fabrication of 3D printed composite membranes with a double-sinusoidal, i.e. wavy, pattern, resulting in enhanced fouling resistance whilst reducing water, chemical cleaning and energy consumption.<sup>2</sup> The 3D composite membrane was obtained by conformal deposition of a thin polyethersulfone (PES) selective layer onto a 3D printed wavy support. Flat (non-patterned) and wavy (patterned) 3D composite membranes were characterised and tested in terms of permeance, rejection, and anti-fouling property using oil-in-water emulsions and by filtering Bovine Serum Albumin (BSA) through a cross-flow ultrafiltration set-up. CFD simulations in terms of velocity profile, local surface shear rate, and transmission probability were used to optimise the design of the wavy pattern and the experimental observations. Results revealed that the wavy composite membrane had significantly higher permeance recovery compared to the flat one, with negligible irreversible fouling and rejection >96% for both oil and BSA. The wavy 3D composite membranes maintained the same level of permeation after 10 complete filtration cycles, using only pure water as cleaning agent. 1. Low, Z.-X.; et al., *J Mem Sci* 2017, 523, 596-613. 2. Al-Shimmery, A.; et al., *J Mem Sci* 2019, 574, 76-85.

**TUESDAY 3:00 pm** - Ballroom 4

**22c - Next-Generation Membranes Using Thin-Film Lift Off**

Mackenzie Anderson (UCLA)\*, Brian McVerry (UCLA), Na He (UCLA), Eric Hoek (UCLA), Richard Kaner (UCLA)

For the past 30 years, thin-film membrane composites have been the state-of-the-art technology for reverse osmosis, nano- and ultrafiltration, and gas separation. However, traditional membrane casting techniques, such as phase inversion and interfacial polymerization, limit the types of material that are used for the membrane separation layer. Here we describe a novel thin-film lift off (T-FLO) technique that enables the fabrication of thin-film composite membranes with new materials for desalination, organic solvent nanofiltration, and gas separation. The active layer is cast separately from the porous support layer, allowing for the tuning of the thickness and chemistry of the active layer. A fiber-reinforced, epoxy-based porous support layer is then cured on top of the active layer that forms covalent bonds between the layers. Upon submersion in water, the cured membrane lifts off from the substrate to produce a robust, free-standing asymmetric membrane composite. We demonstrate the fabrication of three novel T-FLO membranes for chlorine-tolerant reverse osmosis, organic solvent nanofiltration, and gas separation. The isolable nature of support and active layer formation paves the way for the discovery of the transport and selectivity properties of new polymeric materials. This work introduces the foundation of T-FLO membranes, which enables exciting new materials to be implemented as the active layers of thin-film membranes, such as high performance polymers, 2-D materials, and metal-organic frameworks.

**TUESDAY 3:30 pm** - Ballroom 4

**22d - Interfacial Junctions Control Electrolyte Transport Through Charge-Patterned Membranes**

Feng Gao (University of Notre Dame), Bill Phillip (University of Notre Dame)\*

Unique transport mechanisms emerge when nanostructured substrates are patterned with multiple chemistries. For example, due to their charge-patterned structure, charge mosaic membranes are capable of transporting whole salts more rapidly than neutral molecules of comparable or smaller sizes. Here, we elucidate the molecular interactions that promote the transport of whole salts through patterned membranes by using ink jet printing to create a family of membranes with systematically varying the pattern geometry and size. For patterns that consist of equivalent areal coverages of positively-charged and negatively-charged domains, the effects of these geometric parameters were encapsulated in a single variable, the interfacial packing density, that quantified the fraction of the membrane surface covered by junctions between oppositely-charged domains. Experimentally, the transport of symmetric electrolytes (i.e., KCl and MgSO<sub>4</sub>) increased with the value of the interfacial packing density, while the interfacial packing density did not affect the transport of asymmetric electrolytes (i.e., K<sub>2</sub>SO<sub>4</sub> and MgCl<sub>2</sub>). Simulations demonstrate that for symmetric electrolytes, the structural charge heterogeneity reduces the barrier to ion partitioning thereby promoting salt transport. For asymmetric electrolytes, the charge heterogeneity skews the local availability of ions from the stoichiometric ratio of the salt thus hindering salt transport. These findings demonstrate the promise of accessing new transport mechanisms that could revolutionize chemical separations and sensing applications through chemical-patterning of membranes.

**TUESDAY 4:00 pm** - Ballroom 4

**22e - Fabrication of Inside-Out Isoporous Hollow Fiber Membranes via Spinning and Coating Methods**

Kirti Sankhala (Helmholtz-Zentrum Geesthacht, Geesthacht)\*, Joachim Koll (Helmholtz-Zentrum Geesthacht, Geesthacht), Maryam Radjabian (Helmholtz-Zentrum Geesthacht, Geesthacht), Clarissa Abetz (Helmholtz-Zentrum Geesthacht, Geesthacht), Volker Abetz (Helmholtz-Zentrum Geesthacht, Geesthacht)

Isoporous block copolymer membranes enable to tailor the selective surface with promising energy-efficient separations.<sup>1-3</sup> The membranes are fabricated via evaporation-induced self-assembly of block copolymers and non-solvent induced phase separation (SNIPS).<sup>2</sup> The isoporous block copolymer membranes were first reported in flat sheet geometry and afterwards the self-assembled structures were achieved on the outer surface of hollow fibers.<sup>2,3</sup> Self-supported hollow fiber membrane geometry provides a higher active surface area for lesser volume.<sup>3,4</sup> So far, evaporation under normal environmental conditions has been a common approach to achieve microphase separation of block copolymers resulting in regular self-assembled structure. Our recent works introduced a novel approach of controlling the kinetics of microphase separation of block copolymers by using gas flow. PS-b-P4VP diblock copolymer solutions were used for fabrication of technologically-relevant inside-out isoporous hollow fiber membranes. Integral asymmetric and composite inside-out isoporous hollow fiber membranes of inner diameter ca. 1 mm were fabricated by spinning and coating processes, respectively.<sup>5,6</sup> This novel approach of controlled evaporation via gas flow seems the only feasible way to achieve evaporation-induced self-assembly in compact geometries. [1] V. Abetz. *Macromolecular Rapid Communication* 2015, 36:10. [2] K.-V. Peinemann, V. Abetz, P.F.W. Simon. *Nature Materials* 2007, 6:992. [3] M. Radjabian, J. Koll, K. Buhr, U. Vainio, C. Abetz, U.A. Handge, V. Abetz. *Polymer* 2014, 55:2986. [4] K. Sankhala, D. C. F. Wieland, J. Koll, M. Radjabian, C. Abetz, V. Abetz. *Nanoscale* 2019, DOI: 10.1039/C8NR06892E [5] K. Sankhala, J. Koll, M. Radjabian, U. A. Handge, V. Abetz. *Advanced Materials Interfaces* 2017, 4:1600991. [6] K. Sankhala, J. Koll, V. Abetz. *ACS Macro Letters* 2018, 7:840.

**TUESDAY 4:30 pm** - Ballroom 4

**22f - Empirical evidence suggests that polyamide film formation during interfacial polymerization in thin film composite (TFC) membranes is not self-limiting**

Kasia Grzebyk (University of North Carolina at Chapel Hill)\*, Orlando Coronell (University of North Carolina at Chapel Hill)

Thin-film composite (TFC) membranes used in reverse osmosis typically have a polyamide active layer formed by interfacial polymerization (IP) between monomers m-phenylenediamine (MPD) and trimesoyl chloride (TMC). In IP, a support layer containing an aqueous MPD solution makes contact with TMC in an organic solvent. The monomers meet at the aqueous/organic interface, where MPD diffuses into the organic solvent and reacts with TMC to form the polyamide. It is commonly thought that MPD and TMC react to form a film so dense that MPD passage into the organic phase is restricted, thereby terminating polyamide growth. Variations can be employed in IP to alter the polyamide, but regardless of the variation, TFC polyamide layers exhibit a typical maximum thickness of ~200 nm. It is, therefore, believed that IP is self-limiting (Chai and Krantz, 1994, *J Membr Sci*, 93, 175-192; Cahill et al, 2008, *MRS Bull*, 33, 27-32). However, in recent work, Ukrainsky and Ramon (*J Membr Sci*, 2018, 566, 329-335) promoted IP in a microfluidic flow cell and found that IP proceeded so long as monomers were supplied; films grew orders of magnitude thicker compared to conventional TFCs. Accordingly, we investigated the self-limiting quality of IP in TFC membrane fabrication. Our results show that MPD can permeate the active layer of the four TFCs tested. In cross-flow filtration, MPD passage was 22.3%, 4.1%, 3.5%, and 2.8% for NF90, ESPA3, SW C<sub>4</sub>+ and hand-cast TFC membranes, respectively. Furthermore, a method for additional polyamide formation atop TFC membranes was established, where membranes are exposed to a continuous source of MPD during IP. Resulting polyamide thicknesses were ~10x greater than that of conventional TFCs. Our findings indicate that IP terminates due to MPD depletion during IP, not due to its inability to penetrate the polyamide. Our work therefore suggests that novel IP protocols may be developed to produce TFCs with enhanced performance.

**WEDNESDAY 9:30 am** - Kings Garden 4

**23a - Creation of well-defined "mid-sized" micropores in carbon molecular sieve membranes for organic solvent separations**

Yao Ma (Georgia Institute of Technology)\*, Dhaval Bhandari (Exxon Mobil), JR Johnson (Exxon Mobil), Ryan Lively (Georgia Institute of Technology)

Carbon molecular sieve (CMS) membranes are promising candidates for the separation of organic molecules due to their stability, ability to be scaled to practical form factors, and the avoidance of expensive supports or complex multi-step fabrication processes. A critical challenge is the creation of "mid range" (e.g., 5-9 Å) microstructures that allow for both facile permeation of organic solvents and selection between similarly-sized guest molecules. Here, we create these microstructures via the pyrolysis of a microporous polymer (PIM-1) under low concentrations of H<sub>2</sub> gas. The introduction of hydrogen inhibits aromatization of the decomposing polymer network and ultimately results in the creation of a well-defined bimodal pore network with the smallest micropores existing at 5.1 Å. The "H<sub>2</sub>-assisted" CMS membranes show a dramatic increase (~15 times) in p-xylene ideal permeability, while still maintaining commercially attractive p-xylene/o-xylene selectivities when compared to CMS membrane pyrolyzed under a pure argon atmosphere. This technique has the potential to be a platform technique for the creation of CMS microstructures capable of separating a wide variety of organic solvent molecules.

**WEDNESDAY 10:00 am** - Kings Garden 4

**23b - PoreDesigner for computational optimization of channel proteins and porous organic cages for highly selective membrane-based separations**

Ratul Chowdhury (Penn State University)\*

Monodispersed angstrom-size pores embedded in a suitable matrix are promising for highly selective membrane-based separations. They can contribute to energy savings in water treatment and small molecule bioseparations. Aquaporin-based membranes are commonplace in biological membranes to this end, but their low structural stability, modest selectivity and non-tunable selectivity thwarts their applicability as synthetic industrial membranes. We have developed PoreDesigner, a fully automated workflow to redesign the robust beta-barrel Outer Membrane Protein F as a scaffold to access three specific pore designs that exclude solutes larger than sucrose (>360 Da), glucose (>180 Da), and salt (>58 Da) respectively. PoreDesigner further enables us to design any specified pore size (spanning 3-10Å), engineer its pore profile, and chemistry. These redesigned pores may be ideal for conducting sub-nm aqueous separations with permeabilities exceeding those of classical aquaporin-based biological water channels, by more than an order of magnitude at over 10 billion water molecules per channel per second. The versatility of PoreDesigner is not limited to designing water channel proteins and is being used to design channel proteins for DNA sequencing. In other efforts, tools have been developed to simulate and explain the biophysics of water permeation and complete salt rejection through porous pillar-appended pillar[4]arene (PAP4) cages immobilized in biomimetic membranes. The in silico approach was used to assess the energetics, stability, and lowest energy structure of a bouquet of such channels whose unique interlaced organization offered a low-activation salt-rejecting continuous water path with water permeabilities of billion molecules per second.

**WEDNESDAY 10:30 am** - Kings Garden 4

**23c - Crack-free, large-area, single-layer graphene membranes with a record performance in gas mixture separation**

Shiqi Huang (L'Ecole polytechnique fédérale de Lausanne)\*, Kumar Varoon Agrawal (L'Ecole polytechnique fédérale de Lausanne), Jing Zhao (L'Ecole polytechnique fédérale de Lausanne)

Among the emerging membrane platforms, single-layer graphene based membranes are highly promising attributing the atomic thickness. As a result, they have been acclaimed as the ultimate gas separation membrane, capable of yielding ultrahigh gas permeance and an attractive molecular selectivity [1]. However, the development of these membranes face two major bottlenecks: 1) crack-free fabrication of large-area membranes; 2) incorporation of high-density of size-selective nanopores. Herein, we report novel approaches to address these bottlenecks achieving a record separation performance from a relatively large-area graphene membrane [2,3]. The mechanical strength of single-layer graphene was increased by reinforcing it with 100-nm-thick nanoporous carbon film, which eliminated crack formation in the suspended graphene domains even on macroporous supports with 5- $\mu\text{m}$ -sized support pores. A high pore-density ( $2.1 \times 10^{12}$  pores/cm<sup>2</sup>) with a tight pore-size-distribution was incorporated by a novel decoupled pore-nucleation and pore-expansion strategy using a combination of oxygen plasma and ozone that reduced the concentration of pores larger than 0.38 nm to 22 ppm, resulting in a record gas mixture separation performance ( $\text{H}_2$  permeance of 1340 to 6045 GPU;  $\text{H}_2/\text{CH}_4$  separation factor of 15.6 to 25.1;  $\text{H}_2/\text{C}_3\text{H}_8$  separation factor of 38.0 to 57.8) [3]. Implementation of these strategies in a homemade novel millisecond reactor led to attractive  $\text{CO}_2/\text{CH}_4$  separation factor of 18. The membranes were stable at high temperature (150 °C) and could withstand transmembrane pressure difference of 7 bar. Overall, we report the first successful implementation of single-layer graphene film in gas mixture separation and demonstrate that graphene based membranes are indeed capable of reaching the predicted high performance in gas separation. References 1. Wang et al., Nat. Nanotechnol., 2017, 12 (6), 509. 2. Huang et al., Nat. Commun., 2018, 9, 2632. 3. Zhao et al., Sci. Adv., 2019, 5, eaav1851.

**WEDNESDAY 11:00 am** - Kings Garden 4

**23d - Unprecedented  $\text{CO}_2/\text{H}_2$  Selectivity and  $\text{CO}_2$  Permeance Demonstrated in Facilitated Transport Membranes with Tunable Amine- $\text{CO}_2$  Chemistry**

Yang Han (Ohio State University)\*, Winston Ho (Ohio State University)

$\text{CO}_2$ -selective, amine-containing facilitated transport membranes are of great interest for syngas purification since high-pressure  $\text{H}_2$  can be retained upon  $\text{CO}_2$  removal. A variety of amine-containing polymers have shown decent chemical and thermal stability at aggressive conditions, but their  $\text{CO}_2/\text{H}_2$  separation properties are largely limited by the hydrostatic compaction and severe carrier saturation associated with the high syngas pressure. Herein, we report a new approach to enhance the  $\text{CO}_2$  permeability by manipulating the steric hindrance of the amine carriers. A series of  $\alpha$ -aminoacids with different alkyl or hydroxyethyl substituents are deprotonated by 2-(1-piperazinyl)ethylamine, leading to involatile amine carriers with different degrees of steric hindrance. For hosting the low MW amine carriers, a crosslinked and water-swallowable polymer network is synthesized from polyvinylalcohol and polyvinylamine. In order to avoid membrane compaction, perforated graphene oxide mono-sheets are dispersed as reinforcement fillers. In the presence of moisture, a bulkier alkyl substituent to the amino site (increasing steric hindrance) destabilizes the carbamate adduct and thus drastically increases the chemisorption of  $\text{CO}_2$ , while the incorporation of ethylene oxide groups provides additional physisorption of  $\text{CO}_2$ . The enhanced  $\text{CO}_2$  solubility significantly mitigates the carrier saturation behavior, and an unprecedented  $\text{CO}_2/\text{H}_2$  selectivity greater than 100 is demonstrated at 107°C and 12.5 atm of  $\text{CO}_2$  partial pressure. As the  $\text{CO}_2$  partial pressure reduces to 0.4 atm, a less hindered amine yields a higher reactive diffusivity of  $\text{CO}_2$ , resulting in a  $\text{CO}_2$  permeance of 435 GPU with a selectivity greater than 500. The performances of these reaction-mediated polymeric membranes are well above the theoretical upper bound, and they open up a new avenue for designing a highly-selective membrane process for syngas purification.

**WEDNESDAY 11:30 am** - Kings Garden 4

**23e - Engineering the Nanochannels in Reduced Graphene Oxide Membrane for Dye Desalination**

Liang Huang (The State University of New York at Buffalo)\*, Haiqing Lin (The State University of New York at Buffalo)

Graphene and its derivatives, graphene oxide (GO) and reduced graphene oxide (rGO), are excellent platforms for developing size-selective membranes because of their atomic thickness, high mechanical strength, and chemical inertness. However, they usually show moderate rejections for salt ions and high rejections for various dye molecules. Therefore, they are not applicable for dye desalination, which is a big challenge in textile wastewater treatment and involves the separation of dyes from salts (NaCl, Na<sub>2</sub>SO<sub>4</sub>). On the other hand, commercial nanofiltration (NF) and ultrafiltration (UF) membranes are also not efficient in dye desalination, because NF membranes will reject both divalent salts and dyes, while UF membranes have a low rejection for dye molecules. Here we prepared solvated rGO membranes by filtrating rGO dispersion through Nylon microfiltration films. The filtration process was stopped immediately as the rGO dispersion in filter disappeared, while the membrane was still wet, which is the critical step to retain high water flux and strong size-sieving ability. The nanochannel size in solvated rGO membranes is smaller than the sizes of most dye molecules (such as Direct Red 80) and larger than those of divalent salts. So the solvated rGO membranes can reject about 99.0% of Direct Red 80 while showing almost 0% rejection for Na<sub>2</sub>SO<sub>4</sub>. Interestingly, we found that the nanochannels in solvated rGO membranes can be narrowed in salt solutions, which was proven by measuring their molecular weight cutoff (MWCO) curves in 60 g/L Na<sub>2</sub>SO<sub>4</sub> solution. As a result, the solvated rGO membranes exhibited higher dye rejection (99.9% for Direct Red 80) in 60 g/L Na<sub>2</sub>SO<sub>4</sub> solution with almost zero rejection for Na<sub>2</sub>SO<sub>4</sub>. More importantly, their pure water permeance is as high as 80 L/m<sup>2</sup>·h·bar, which is about 8 times that of NF membranes and 2 times that of UF membranes (MWCO: 2000), suggesting their promise for practical applications in dye desalination.

**WEDNESDAY 12:00 pm** - Kings Garden 4

**23f - Impact of module design on heat transfer and Nusselt correlation selection in membrane distillation**

Alexander V Dudchenko (Carnegie Mellon University)\*, Meagan S Mauter (Carnegie Mellon University)

Membrane distillation (MD) is a thermally driven process that can treat high salinity waters utilizing low grade heat or renewable sources, making it an attractive low cost treatment process for heavily impaired waters (e.g. waste brines, produced water, saline ground waters). The driving force in MD process (flux, water recovery) is governed by the heat transfer to/away from the membrane surface, which if poorly estimated can lead to an inaccurate process performance prediction. Although, the effect of flow channel design, fluid flow rates, and thermophysical properties has been well understood in heat exchanger design, leading to development of over a dozen empirical Nusselt correlations, these relationships have not been validated in MD. Here, we present a novel approach that leverages our fundamental understanding of vapor transport and energy transfer through the membrane, removing need for high accuracy equipment for estimation of heat transfer rates. Using this method, we demonstrate how module design (e.g. length, width) impacts heat transfer in experimental modules and apparent membrane performance. We further extend the method to allow quantitative validation of existing Nusselt correlations. Utilizing a rich experimental data set for open and spacer filled channels we demonstrate how validity of these correlations changes across different module designs, providing guidance for accurate correlation selection.

**WEDNESDAY 9:30 am** - Kings Garden 3

**24a - Experimental and Theoretical Investigations of the Loss of Protein Sieving Due to Fouling of ATF Microfilters**

Alex Apostolidis (Amgen)\*, Glen Bolton (Amgen)

A prevalent technology to enable perfusion in cell culture processes is alternating tangential flow (ATF) filtration. ATF operations can be limited by sieving loss due to membrane fouling. In this study, ATF filters were fouled using a range of levels of a model cell lysate stream and antibody sieving was measured as a function of processing time. The sieving of antibody through filters with different fiber lengths or diameters were studied using the model stream. The effects of feed and permeate flux were investigated. The results suggest that sieving can be improved using conditions that lead to higher membrane sweeping and backflow: longer fibers, smaller diameter fibers, higher feed flow rate, and lower permeate flow rates. The results were well described by theoretical models that were recently developed to capture the physics behind microfilter fouling. The results were then confirmed in bioreactor experiments with model solution and cell culture. These observations can lead to operational improvements that can improve the yield and robustness of ATF filtration.

**WEDNESDAY 10:00 am** - Kings Garden 3

**24b - pH and Excipient Partitioning in Ultrafiltration / Diafiltration Processes for Formulation of High Concentration Monoclonal Antibody (mAb) Products**

Parinaz Emami (Penn State University)\*, Youngbin Baek (Penn State University), Nripen Singh (Bristol-Myers Squibb), Andrew Zydney (Penn State University)

Ultrafiltration (UF) and diafiltration (DF) are used for the final formulation of monoclonal antibody therapeutics, placing the product into the desired buffer at the target concentration. A number of studies have demonstrated that the pH and excipient / salt concentration at the end of the DF can be significantly different than that in the DF buffer, but there are still significant uncertainties over the origin of these phenomena. The objective of this study was to develop a mass balance model to describe the pH and excipient profiles throughout the UF/DF process accounting for the effects of Donnan equilibrium, buffer-protein and protein-protein interactions. Experimental studies were performed with two mAbs provided by Bristol-Myers Squibb. UF and DF were conducted using Pellicon® 3 TFF Cassettes with 30 kDa Ultracel membranes (MilliporeSigma). The DF was performed from a phosphate buffer into a low ionic strength histidine buffer, in some cases followed by concentration up to 200 g/L by UF, with the solution pH and histidine concentration evaluated over the course of the process. There was a small increase in pH during the initial stage of the diafiltration even though the feed and DF buffer were both at pH 7. This increase in pH was due to the shift in effective buffer pKa due to the reduction in ionic strength. The pH over the latter portion of the DF was determined by the mAb charge via Donnan equilibrium effects, with the final pH being below that in the DF buffer for a negatively-charged mAb and above that for a positive mAb. The pH continued to change during the final UF due to a combination of Donnan effects and the change in mAb charge with increasing mAb concentration associated with intermolecular electrostatic interactions between the proteins. Model calculations were in good agreement with the experimental data during both DF and UF, providing a framework for the design and optimization of UF/DF processes to achieve the desired mAb formulation.

**WEDNESDAY 10:30 am** - Kings Garden 3

**24c - Effect of membranes molecular weight cut-off on peptides migration and selectivity during electro dialysis with filtration membranes**

Sabita Kadel (Laval University)\*, Jacinthe Thibodeau (Laval University), Carole Laine (Amer-Sil), Laurent Bazinet (Laval University)

Filtration membranes (FM) are an integral part of electro dialysis with filtration membranes (EDFM); therefore, their properties have significant impact on peptide separation and overall performance. Thus, the objective of this study was to understand the effect of FM properties (MWCO, porosity, pore size distribution, surface charge, contact angle, etc.) on global and selective peptides migration to the anionic (A-RC) and cationic (C+RC) peptides recovery compartments. In this study, six polyether sulfone (PES) FM with different molecular weight cut-offs (MWCO) of 5, 10, 20, 50, 100 and 300 kDa were used to separate peptides from complex whey protein hydrolysate. As expected, global migration rate of peptides to both recovery compartments was the lowest for 5 kDa (A-RC= 2.41±0.34g/m<sup>2</sup>·h, C+RC=3.19±0.15g/m<sup>2</sup>·h) and the highest for 300 kDa (A-RC= 11.28±1.40g/m<sup>2</sup>·h, C+RC=10.92±1.65g/m<sup>2</sup>·h): the migration rate as a function of MWCO increased in linear way. Surprisingly, the relative abundance of identified cationic peptides migrating to C+RC through studied FMs were found to be similar. However, in A-RC, the relative abundance of negatively charged peptides, notably the lower molecular mass peptides IDALNENK (MW=915.4661 Da) & VLVLDTDYK (MW=1064.5753 Da) was the highest for 5 and 10 kDa. On the other hand, the relative abundance of highly negatively charged peptides with higher molecular mass TPEVDDEALEK (MW=1244.5772 Da) & VYVEELKPTPEGDLEILLQK (MW=2312.2515 Da) increased with an increase in MWCO. These results indicate that MWCO as well as FM properties such as surface charge, porosity, and pore size distribution have significant impact on the selective migration of anionic peptides but no effect on cationic peptides when negatively charged FM (PES) were used.

**WEDNESDAY 11:00 am** - Kings Garden 3

**24d - Scale down depth filtration case study using Pall Supracap™ 50 to predict large scale STAX™ capacity and product quality**

Patricia Rose (Merck Pharmaceuticals)\*, Jennifer Pollard (Merck Pharmaceuticals)

Depth filtration is commonly used as either the primary or secondary step in mammalian cell culture harvest. Early key data to predict filter capacity, processing time and product quality could be generated from small scale cell culture batches if a robust filtration scale down model is available. However there are inherent issues with scale down filtration. While process parameters such as flux can be maintained across scales, there are limitations to aligning equipment and membrane module geometry. Also the cell culture; cell density, cell viability, debris and media, can have different responses at different scales. Slight differences in flow path and membrane configuration can change how the cells interact with each other and the filtration media. The cells can settle and/or become damaged differently compared to large scale. These inconsistencies can impact the small scale depth filter capacity to either significantly over or under forecast the filtration requirements for large scale. This paper will present a scale down model case study using the Pall Supracap™ 50 depth filter to predict performance of the Pall STAX™. Scale down strategy qualification and using direct translation of operating parameters or matching pressure profiles will be discussed.

**WEDNESDAY 11:30 am** - Kings Garden 3

**24e - Unraveling the Plugging Mechanisms during a Combined Tangential-flow and Depth Filtration Process**

Xianghong Qian (University of Arkansas)\*, Da Zhang (University of Arkansas), Daniel Strauss (Asahi Kasei), Parag Patel (Asahi Kasei), Ranil Wickramasinghe (University of Arkansas)

The rapid advancement in upstream cell culture operations has led to a significant increase in product titers. However, this high-level of productivity is accompanied by a rather high cell density which places a significant burden on the traditional downstream clarification and purification operations, especially during the initial clarification and capture steps. Depth filtration, centrifugation and tangential-flow filtration (TFF) have been used to remove cells, cell debris and other impurities. Depth filter consists of a thick porous bed that can trap particles within the filter in contrast to screen type filters that largely reject particulate matter based on surface filtration. On the other hand, the tangential flow of the feed to the membrane surface leads to the suppression of cake growth during TFF operation. BioOptimal MF-SL from Asahi KASEI operates as a hybrid TFF-depth filter. However, the plugging mechanism(s) for BioOptimal MF-SL and other hybrid filters are poorly understood. Here a combined pore blockage and cake filtration model has been able to describe well the fouling mechanism of this hybrid filter in the normal flow mode whereas a resistance in series model has been able to predict performance of the filter operated in the TFF mode. Significant insights have been obtained in understanding the fouling mechanism and optimal operation condition of this hybrid filter.

**WEDNESDAY 12:00 pm** - Kings Garden 3

**24f - Functionalized Microporous Membranes for Protein Capture and Analysis**

Joshua Berwanger (University of Notre Dame)\*, Merlin Bruening (University of Notre Dame), Liu Yang (University of Notre Dame), Hui Yin Tan (University of Notre Dame), Weijing Liu (University of Notre Dame)

Microporous membranes are an attractive alternative to resins for protein affinity capture, especially for protein identification and quantification. Convective flow through micron-sized pores in membranes minimizes diffusion limitations to allow protein binding in short residence times. Derivatization of micropores with poly(acrylic acid) introduces -COOH groups for simple functionalization with a range of affinity molecules. Moreover, the poly(acrylic acid) films show low nonspecific adsorption. This talk highlights the use poly-electrolyte modified membranes for purification of His-tagged proteins, binding and analysis of therapeutic monoclonal antibodies, and immobilization of small-molecule drugs for determination of their protein targets. Functionalization of membranes with Ni-NTA complexes enable purification of polyhistidine-tagged proteins in minutes when using a spin membrane format. Immobilized mimotopes (epitope-mimicking peptides) selectively capture therapeutic monoclonal antibodies out of serum enabling quantitation and analysis. Recent work is exploring the immobilization of small-molecule drugs to identify intended and unintended protein targets. Initial reflectance FTIR studies allow rapid screening to develop the immobilization conditions that lead to minimal nonspecific adsorption. In summary, functionalized microporous membranes can accomplish affinity capture of various proteins more quickly and efficiently than bead-based methods.

**WEDNESDAY 9:30 am** - Ballroom 3

**25a - A systematic approach to remove bottlenecks in high concentration UF/DF for subcutaneous application of biological drug substances**

Hasin M Feroz (Bristol-Myers Squibb)\*, Dongyoun Jang (Bristol-Myers Squibb), Jessica Hung (Bristol-Myers Squibb), Yan Chen (Bristol-Myers Squibb), Erinc Sahin (Bristol-Myers Squibb), Andrew Zydney (Penn State University), Melissa Holstein (Bristol-Myers Squibb), Sanchayita Ghose (Bristol-Myers Squibb)

The current industry focus on subcutaneous administration of biological drug products necessitates purified mAb at concentrations of ~100 g/L, more than an order of magnitude higher than those used for most intravenous applications. However, UF/DF-based (ultrafiltration / diafiltration) approaches to buffer exchange and concentrate to high concentrations poses specific challenges from an operational, formulation, and molecular stability perspective. We identify these challenges and propose strategies to remove the bottlenecks for high concentration UF/DF applications. Most notable challenges of high concentration operations are identified as 1) high pressures exceeding safety limits in current UF/DF devices due to exponential increase in viscosity at high mAb concentrations, 2) recovering high yields of the concentrated drug substance from the system with minimal dilution, and 3) throughput and material loss during post UF/DF sterile filtration. Mitigation strategies include the use of viscosity-modifying excipients at high concentrations, investigating UF/DF devices with modified membranes and/or improved flow channel design to address pressure concerns at higher concentrations, as well as implementing a low flux plug-flow flush strategy to recover the concentrated drug substance from the hold-up volume of the UF/DF skid at minimal dilution. From a formulation perspective, we are challenged with higher aggregation rates at high protein concentrations, due to higher frequency of intermolecular interactions. We also investigated larger differences in pH and excipient concentrations (diafiltration buffer vs retentate composition) during both diafiltration and ultrafiltration as a function of isoelectric point and concentration of proteins, buffer, pH and excipient concentrations. Our findings suggest that protein concentration plays an important role in protein stability as well as the accuracy of chemical composition of the final formulation.

**WEDNESDAY 10:00 am** - Ballroom 3

**25b - Continuous Diafiltration for cGMP Biomanufacturing**

Akshat Gupta (MilliporeSigma)\*, Beth Goodrich (MilliporeSigma), Herb Lutz (MilliporeSigma)

Diafiltration is a critical unit operation which is part of practically every downstream purification train of monoclonal antibody or bio therapeutic modality production. It is typically employed to provide an efficient and robust method for exchanging buffer matrix for the therapeutic modality and offers simultaneous clearance of small molecule and elemental impurities. Continuous manufacturing and process intensification approaches has been an area of keen interest and various technologies are being investigated to make biotherapeutic manufacturing process more efficient in terms of facility utilization and capital cost reduction by reducing reliance on large scale facilities. Technologies like multi-column cycling, inline viral inactivation and single pass tangential flow filtration (SPTFF) for protein concentration have been developed in past few years, offering significant improvement over their existing batch equivalents. Ability to develop a similar technology for diafiltration suitable for GMP manufacturing has remain rather elusive. Our approach here is based on a shift in perspective wherein the process design is based on membrane utilization and system footprint as opposed to flux and process time in a typical batch diafiltration process. This rather flexible technology offers 6-8-fold increased membrane utilization, up to 3-fold reduction in pump passes and system footprint can be substantially decreased. Buffer usage, extent of buffer exchange, and product yield are consistent with a constant volume diafiltration process. In this presentation, we will present a system design for this concept and a 24-hour experimental data demonstrating operational robustness. Implementation into a fully continuous, or intensified process train and flexibility of the system to accommodate complex diafiltration schemes for challenging molecules will also be discussed.

**WEDNESDAY 10:30 am** - Ballroom 3

**25c - Understanding the role that patterning plays on membrane biofouling by visualization using light imaging and simulation**

Anna Malakian (Clemson University)\*, Bowen Ling (Stanford University), Ilenia Battiato (Stanford University), Scott Husson (Clemson University)

The goal of this project is to develop the basic science needed to design new fouling-resistant membranes. We present findings on the relationship between membrane surface patterning and protein fouling that support two hypotheses (i) geometric patterns will reduce membrane fouling compared to the control, and (ii) computational models will accelerate the discovery of new membrane surface morphologies and methods to improve membrane fouling resistance. Experimental efforts combined flux decline measurements with light microscopy to study the fouling of as-received and patterned polyethersulfone membranes during ultrafiltration of bovine serum albumin (BSA, model foulant). Patterned membranes were prepared by embossing a "tire-tread" micropattern (TTP) on the surface. Both membrane types were labeled with 5-DTAF. BSA labeled with Alexa Fluor 488 was used to visualize the fouling profiles with confocal laser scanning microscopy (CLSM), which provided three-dimensional images of membrane surface patterns and co-localized protein foulant. In parallel, numerical simulations were used to compare fouling patterns with visual analysis of the CLSM images and to explore the full potential of the TTP. We utilized the customized simulator SUMs (Stanford University Membrane solver) within the OpenFOAM framework. The solver uses a finite volume method to study the dynamic couplings among flow, solute transport, and surface fouling. From the numerical study, we found that the TTP acts as a fouling-focusing mechanism. When the flow alternates, the foulant shifts its preferential accumulation zone and self-cleans the previously fouled region. This innovative design provides a possibility to consecutively alternate flow direction during operation to periodically clean zones of the membrane surface. The overall approach is expected to aid in the design of new membranes with tailored surface structures that prevent the irreversible deposition of foulants in prone-to-foul regions.

**WEDNESDAY 11:00 am** - Ballroom 3

**25d - Treating Poultry Processing Wastewaters by Combined Electrocoagulation and Ultrafiltration**

Ranil Wickramasinghe (University of Arkansas)\*, Kamyar Sardari (University of Arkansas)

Ultrafiltration (UF) is an emerging technology of interest for the treatment of highly impaired industrial wastewaters. The US poultry industry produces over 60 billion gallons of poultry processing wastewater (PPW) requiring treatment. In this work, nine different commercially available ultrafiltration membranes, having different pore sizes (10 to 300  $\mu\text{m}$ ) and made of different polymeric materials (polyethersulfone and regenerated cellulose), were screened for treating PPW streams obtained from bird washer and chiller operations. Bird washer wastewater was found to be more fouling as it contained higher biochemical oxygen demand (BOD), chemical oxygen demand (COD), oil and grease (O & G) and total suspended solid (TSS) compared to the chiller wastewater. The presence of suspended particles can lead to plugging of the membrane pores. Thus, it is of significant importance to select the most appropriate membrane (pore size, polymeric material, flux, etc.) that minimizes the fouling and maximizes contaminant rejection. For the feed streams considered here, membranes with 30 kDa nominal molecular weight cut-off provided the most stable performance in laboratory scale tangential flow filtration. Development of a practical ultrafiltration process will involve pretreatment of the feed stream. Here electrocoagulation (EC) was used to pretreat PPW. EC is shown to be effective in removing suspended solids and organic compounds which foul the membrane. Higher EC reaction times result in higher contaminant removal. We show that EC can remove over 85% of fats, oil and grease and total suspended solids from the PPW. The EC-UF process results in lower flux decline and enhanced contaminant rejection. Finally, long-term EC-UF experiments, were conducted with membrane cleaning, to study the feasibility of the combined process.

**WEDNESDAY 11:30 am** - Ballroom 3

**25e - Mass transfer assisted TIPS process to precisely tailor the hollow fiber membrane surface and sublayer structures**

Hideto Matsuyama (Kobe University)\*, Chuanjie Fang (Kobe University), Saeid Rajabzadeh (Kobe University)

A novel method was used to tailor the surface and sub-layer structure of the poly (vinylidene fluoride) (PVDF) hollow fiber membranes in the TIPS process by the co-extrusion of different types of solvents at the outer layer of the extruded polymeric solution. By changing solvent type, membrane surface structure was controlled in an extensive range, e.g. pore size varied from 24 to 600 nm, and water permeability changed from 3 to more than 4000 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>, with a slight change in the membrane mechanical strength. A slight mass transfer that happened during the air gap distance, before starting phase separation, changed the membrane sublayer structure considerably from a bicontinuous to a composite-like structure, spherulites embedded in the bicontinuous network. The segregation of the diluent molecules or PVDF chains to the interface between the extruded solvent and polymer solution was assessed to tailor the membrane surface and sub-layer structures. The diffusion of extruded solvents with good compatibility to PVDF into the polymer solutions altered the phase separation mechanism and produced a novel composite-like structure in the sub-layer of the membrane. This membrane structure enhanced permeation stability drastically based on its unique structure to dissipate the applied hydrodynamic pressure and resist against the membrane compaction. Mass transfer phenomena at the interface were assessed by using molecular dynamics simulation (MD) to support our proposed explanations. Finally, membrane structures and characteristics are summarized based on the change in the competitive ternary interactions between the polymer, diluent, and extruded solvent. This kind of summarization potentially can be used as a guideline for selecting appropriate extruded solvents to tailor membranes with desired structures and characteristics.

**WEDNESDAY 2:00 pm** - Ballroom 4

**25f - Organic solvent resistant membranes obtain by using non-toxic solvents**

Stefan Chisca (King Abdullah University of Science and Technology)\*, Gheorghe Falca (King Abdullah University of Science and Technology), Tommaso Marchesi (University of Bologna), Valentina Elena Musteata (King Abdullah University of Science and Technology), Suzana Nunes (King Abdullah University of Science and Technology)

Membrane technology is a sustainable process which can replace the conventional separation methods in chemical, pharmaceutical and petrochemical industries [1]. However, the membrane fabrication process involve in general the use of toxic solvents such as DMF and NMP [2]. Therefore, another main challenge of this technology beside to design membranes which are easy to process and are stable in wide range of pH and organic solvents, is to improve the sustainability of membrane fabrication. One way to achieve this is to replace the common toxic solvents with greener ones, such as ionic liquids, which are chemically stable, non-flammable and has relative low toxicity and volatility [3]. In this study we report the synthesis of organic solvent resistant polytriazole membranes by dissolving the polymer in ionic liquid at 85°C. The membranes were obtain by phase inversion method. The resulting solution was cast on a glass plate and then it was immersed after different time in water. To obtain crosslinked polytriazole membranes we exposed them to two different diepox crosslinkers. The performance of the membranes were evaluated in DMF at 20°C, 65°C, 85°C and 105°C. The permeances were in the range of 4 - 10 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup> with the MWCO in the range of 1000 g/mol. We used dynamic mechanical analyzer to correlate the membranes performance with the mobility of the crosslinkers and polytriazole chains and we investigated the mechanical properties by measuring the creep recovery. Moreover we used scanning electron microscopy to investigate the morphology of the membranes before and after filtration at 105°C. Acknowledgment This work was sponsored by King Abdullah University of Science and Technology (KAUST), CRG6 URF/1/3441-01-01. References 1. D.S., Sholl, R.P., Lively, Nature 532, 435-437 2016. 2. G. Szekely, M. F. Jimenez-Solomon, P. Marchetti, J. F. Kim. A. G. Livingston, Green Chem., 16, 4440-4473, 2014. 3. P. C. Marr and A. C. Marr, Green Chem. 18, 105-128, 2016.

**WEDNESDAY 9:30 am** - Ballroom 4

**26a - Artificial Water Channels - toward biomimetic membranes for desalination**

Mihail Barboiu (Institut Europeen des Membranes)\*

This lecture discusses the incipient development of the first artificial water channels systems. We include only systems that integrate synthetic elements in their water selective translocation unit. Therefore, we exclude peptide channels because their sequences derive from the proteins in natural channels. We review many of the natural systems involved in water and related proton transport processes. We describe how these systems can fit within our primary goal of maintaining natural function within bio-assisted artificial systems. In the last part, we present several inspiring breakthroughs from the last decade in the field of biomimetic artificial water channels. All these examples demonstrate how the novel interactive water-channels can parallel biomolecular systems. At the same time these simpler artificial water channels offer a means of understanding water structures useful to understanding many biological scenarios. Moreover they can be used for the preparation of highly selective membranes for desalination. [1] M. Barboiu and A. Gilles, *Acc. Chem. Res.* 2013, 46, 2814-2823. [2] M. Barboiu, *Angew. Chem. Int. Ed.* 2012, 51, 11674-11676. [3] Y. Le Duc, et al., *Angew. Chem. Int. Ed.* 2011, 50(48), 11366-11372. [4] E. Licsandru, et al., *J. Am. Chem. Soc.*, 2016, 138, 5403-5409. [5] M. Barboiu, *Chem. Commun.*, 2016, 52, 5657- 5665. [6] I. Kocsis, et al. *Science Adv.* 2018, 4, eaao5603.

**WEDNESDAY 10:00 am** - Ballroom 4

**26b - Self-Assembly of Long-Lasting Lipid Bilayers and the Effect of Temperature of their Ion Rejection**

Yair Kaufman (Ben Gurion University of the Negev)\*, Shiju Abraham (Ben Gurion University of the Negev), Tabea Heckenthaler (Ben Gurion University of the Negev), Yacov Morgenstern (Ben Gurion University of the Negev)

Supported lipid bilayers have promising potential for diverse separation processes, such as water desalination and small-molecule/ion separation, as well as for biosensors. However, the preparation of long lasting (thermodynamically stable) defectless (no holes) lipid bilayer is challenging, and for some applications, these are crucial requirements. During the talk, I will shed-light on the vesicle fusion mechanism, which is the commonly used mechanism to prepare supported lipid bilayers with or without membranes proteins. Then, based on theoretical analysis and experimental results, I will describe the conditions that render these bilayers thermodynamically stable. Lastly, I will highlight the profound effects of temperature on the resistance of lipid bilayers to ion transport (i.e., ion rejection).

**WEDNESDAY 10:30 am** - Ballroom 4

**26c - Peptoid-based membrane-mimetic 2D nanomaterials with incorporated natural and synthetic channels**

Chunlong Chen (Pacific Northwest National Laboratory)\*

From a materials perspective, cell membranes, which consist of 3.0 - 5.0 nm thick lipid bilayers, provide a great source of inspiration for developing functional 2D nanomaterials because they exhibit sequence-specific water and ion transport and the ability to self-repair. Inspired by that, we recently developed sequence-defined and lipid-like peptoids that self-assembled into highly stable and self-repairable membrane-mimetic 2D materials. These membranes were formed through a solvent-induced crystallization process, in which inter-peptoid hydrophobic interactions drove the anisotropic packing of peptoids to form a bilayer-like membrane structure. They exhibit a number of properties associated with cell membranes, including spontaneous assembly at interfaces and the ability to self-repair. We further demonstrated that these membranes are superior to lipid bilayers and other assembled 2D materials because: 1) they are free-standing, atomically ordered, and highly stable in pure organic solvents, biological environments, as well as high temperature; and 2) a broad range of active functional groups, including chromophores, can be incorporated and patterned within membranes as peptoid side chains. To take advantages of the unique feature of these peptoid membranes, we further demonstrated the incorporation of both natural and synthetic channels into these membranes using the co-crystallization approach. Because peptoids are easy to synthesize, have large side-chain diversity, and offer the unique advantage for controlling self-assembly due to the lack of backbone hydrogen bond donors, we recently demonstrated the introduction of a wide range of channel-forming molecules into these peptoid-based 2D nanomaterials, offering the potential of building artificial channels through peptoid self-assembly.

**WEDNESDAY 11:00 am** - Ballroom 4

**26d - Scalable High-Performance Membranes with High Density Channel Protein-Polymer Nanosheets**

Yu-Ming Tu (Penn State University)\*, Woonchul Song (Penn State University), Tingwei Ren (Penn State University), Yuexiao Shen (UC Berkeley), Ratul Chowdhury (Penn State University), Prasangi Rajapaksha (University of Kentucky), Drew Carson (Penn State University), Yuxuan Dai (Penn State University), Arwa Mukthar (Penn State University), Miaoci Zhang (Penn State University), Alina Thokkadam (Rutgers University), DB Bhattacharyya (University of Kentucky), Bill Phillip (University of Notre Dame), Robert Hickey (Penn State University), Yinai Wei (University of Kentucky), Manish Kumar (Penn State University)

Biological membranes containing channel proteins exhibit high permeability while maintaining high solute selectivity due to transport proteins with well-defined pore geometry and functionality to exclude or pass specific solutes. Nevertheless, membrane protein-based biomimetic membranes studied so far suffer from low protein insertion, the use of vesicular morphologies, and the use of poorly scalable dialysis-based self-assembly procedures in synthesizing such membranes. These challenges have resulted in much lower than anticipated improvements. In this presentation, we will present the development of scalable high-performance biomimetic membranes that are based on densely packed  $\beta$ -barrel channel proteins in block copolymers to create robust and flat nanosheets. These highly packed crystalline structures and well-ordered nanosheets were constructed by an innovative solvent evaporation method that can be completed within 2-hours and further supported on a porous substrate as high-performance selective layers by a modified layer-by-layer technique. Three passive  $\beta$ -barrel channel proteins with inherently narrow and uniform pore sizes of  $\sim 0.5 - 1.5$  nm were tested in this work including a passive outer membrane protein F (OmpF), alpha-hemolysin ( $\alpha$ HL) and a redesigned outer membrane protein mutFhuA (FhuA  $\Delta$ C/ $\Delta$ 4L). OmpF,  $\alpha$ HL and FhuA  $\Delta$ C/ $\Delta$ 4L nanosheet-incorporated membranes maintained their unique molecular selectivity with molecular weight cutoffs of  $\sim 477$ , 927 and 1134 Da respectively, while demonstrating high water permeabilities of 322, 793 and 1092 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>, which are about 20-500 times greater than commercial nanofiltration membranes with comparable molecular exclusion limits. This approach of combining channel proteins and BCPs utilizing the scalable membrane fabrication technique could open new routes in developing high performance biomimetic membranes thus exploiting the exquisite specificity and functionality of various channel proteins.

**WEDNESDAY 11:30 am** - Ballroom 4

**26e - Fabrication of aquaporin-based biomimetic membrane for seawater desalination**

Ye Li (Nanyang Technological University)\*, Rong Wang (Nanyang Technological University)

Aquaporins (AQPs), consisting of a family of water channel proteins, have been adopted to fabricate high performance membranes attributed to their superior water/solute selectivity. This study focuses on enhancing the mechanical strength of aquaporin-based biomimetic membranes for seawater desalination application. Aquaporin incorporated vesicles were embedded into the selective layer of the optimized thin film composite (TFC) membrane. The resultant membrane, denoted as ASW, exhibited a stable water flux around 20 L·m<sup>-2</sup>·h<sup>-1</sup> and 99% NaCl rejection at a constant pressure of 55 bar using 32,000 ppm NaCl solution as feed in reverse osmosis (RO) measurement. The robustness of the ASW membranes were evaluated by measuring the water flux change due to pressure compaction and characterized by Atomic Force Microscope (AFM). The water flux of ASW membrane was almost 100% enhanced compared with that of aquaporin-free control TFC membranes (i.e., a water flux of 11-12 LMH). The filtration performance of the ASW membrane was further evaluated by a seven-day desalination test using a real seawater secondary effluent collected from a desalination plant in Singapore as feed. To our best knowledge, this is the first report on the aquaporin-incorporated RO membrane that can be used for seawater desalination. A commercial SW30HR membrane was tested in parallel for comparison. The robust ASW membrane exhibited a nearly 80% higher water flux in comparison to the SW30HR membrane with a comparable overall solute rejection, suggesting the advantage and feasibility of Aquaporin based biomimetic membranes for seawater desalination.

**WEDNESDAY 12:00 pm** - Ballroom 4

**26f - Biomimetic channel membranes: can they realize their full potential upon scale-up?**

Viatcheslav Freger (Technion - IIT)\*

The unique selectivity and permeability of biological water channels provide much inspiration for developing their synthetic mimics [1]. Recent progress in biomimetic channels has been remarkable and their performance approaches that of commercial reverse osmosis membranes [2]. However, most estimates of the potential performance are based on experiments with individual channels or vesicles or membrane patches of microscopic dimensions. Under such conditions, the concentration polarization (CP) is small, since the boundary layer has a spherical symmetry and its effective thickness is commensurate with the membrane size, which is at least an order of magnitude smaller than in standard membrane operations. As a result, the CP level is apparently negligible in micro-scale experiments and does not interfere with the channel performance. However, the geometry of the diffusion profile will change and CP level increase drastically in macroscopic membranes incorporating densely spaced channel arrays [3]. If not properly addressed in membrane design, the increased CP level in scaled-up channel-based membranes may greatly compromise the observed selectivity and reduce permeation rates due to increased osmotic pressure. Although re-setting the target of selectivity to a much higher value may partly offset this limitation, the presented analysis highlights a major engineering challenge towards scale-up and utilization of the biomimetic channels in next-generation water purification membranes. [1] JR Werber, M Elimelech, *Science Advances* 2018, 4 (6), eaar8266. [2] RH Tunuguntla et al., *Science* 2017, 357 (6353), 792-796; J Abraham et al, *Nat. Nanotechnol.* 2017, 12 (6), 546-550; Z Sun et al., *Faraday Discuss.*, 2018, 209, 113-124; W Song et al., *Faraday Discuss.*, 2018, 209, 193-204 [6] V Freger, *Faraday Discuss.*, 2018, 209, 371

**WEDNESDAY 9:30 am** - Kings Garden 5

**27a - Surface Nano-structuring with Hydrophilic Polymer Brush Layers for Membrane Performance Tailoring and Optimization**

Yian Chen (UCLA)\*, Soomin Kim (UCLA), Anditya Rahardianto (UCLA), Yoram Cohen (UCLA)

Membrane technologies are increasingly used for water treatment and purification to relieve global water scarcity. However, improving reverse osmosis (RO), nanofiltration (NF) and ultrafiltration (UF) membrane performances require one to effectively mitigate membrane fouling and mineral scaling, enable high membrane cleaning efficiency, and ensure high membrane permeability and solute rejection. Surface nano-structuring with tethered hydrophilic polymers is touted as an effective way of rendering membrane surfaces fouling/scale resistance while facilitating effective membrane cleaning with freshwater, thereby avoiding/reducing the need for chemical cleaning agents. In order to synthesize membranes with tethered hydrophilic polymers surface activation of the base membrane can be accomplished with Atmospheric Pressure Plasma-induced Graft Polymerization (APPIGP), followed by free radical graft polymerization. The above approach was investigated in the present work aiming to both optimizing membrane surface properties and correlating surface structure and interfacial interactions with (a) alteration of RO/NF and UF membrane characteristics and performance due to tethered polymer chains formed by APPIGP; (b) RO/NF and UF membrane fouling and cleaning mechanisms, and (c) scaleup of the process for production of high-performance spiral-wound RO/NF elements for a range of desalination applications.

**WEDNESDAY 10:00 am** - Kings Garden 5

**27b - Roughness in Polyamide RO Membranes: Its Formation Mechanism, Control, and Implications**

Chuyang Y Tang (University of Hong Kong / University of New South Wales)\*

Water scarcity is one of the major global challenges of our time. Reverse osmosis technology plays a crucial role in providing alternative sources of water through seawater desalination and water reclamation. Thin film composite polyamide membranes are the gold standard for reverse osmosis technology, but tuning their permeability and selectivity remains a major challenge because of the inherent permeability-selectivity trade-off. The polyamide rejection layer of a typical reverse osmosis membrane contains a large number of discrete nano-sized voids occupying as much as 30% of its total volume. Despite the common belief that these nanovoids regulate the membrane water permeability and salt rejection, little is known about their formation mechanism. In this presentation, we show that these nanovoids are formed due to the degassing of nanobubbles from the monomer solution during the interfacial polymerization process to fabricate the polyamide selective film. Simple nano-foaming methods, such as addition of sodium bicarbonate and ultrasound application, can result in remarkable improvement in both membrane water permeability and salt rejection, thus overcoming the long-standing permeability-selectivity trade-off of desalination membranes. Our study further establishes a framework for the fundamental understanding of the structure-property-performance relationship of polyamide desalination membranes.

**WEDNESDAY 10:30 am** - Kings Garden 5

**27c - Mechanism of chlorine attack on polyamide membranes studied by EIS**

Mikhail Stolov (Technion - IIT), Viatcheslav Freger (Technion - IIT)\*

The well-known and yet incompletely understood Achilles heel of polyamide membranes is low tolerance to chlorine. Much information on the chemical mechanism and transformations that take place upon chlorine attack has been obtained by post-mortem spectroscopic analytical methods, which limited the sensitivity and temporal resolution of the kinetic analysis. As an alternative method that may directly probe variations of transport characteristics and ion rejection properties of polyamide layer in real time and for low chlorine doses, we employed electrochemical impedance spectroscopy (EIS) to investigate the mechanism and kinetics of chlorine attack. In this way, we could focus on early stages of the chlorination and low chlorine concentrations (15 to 197 ppm). EIS results partly conform to established two-stage mechanism that proceeds as N-chlorination followed by either C-chlorination in acidic conditions or amide bond scission in alkaline conditions. However, early-time kinetics in acidic conditions shows inconsistencies with this model and is best explained by direct ring chlorination that proceeds in parallel to (reversible) N-chlorination, possibly obscured by a finite rate of polymer relaxation. The data also indicate that N-chlorination reduces membrane polarity and ion permeation, yet its effect is eventually reversed by C-chlorination that has an opposite effect. Thereby, the ultimate chemical transformations (C-chlorination at low pH or amide bond cleavage at high pH) result in an irreversible increase in membrane polarity and loss of ion rejection. The results highlight the potential of EIS as a powerful and sensitive tool that may assist in assessing membrane stability and developing new chlorine-resistant membranes [1]. [1] M. Stolov, V. Freger, Degradation of polyamide membranes exposed to chlorine: an impedance spectroscopy study, Environ. Sci. Technol., in press, DOI: 10.1021/acs.est.8b04790

**WEDNESDAY 11:00 am** - Kings Garden 5

**27d - Physicochemical and electrochemical characterization of cation-exchange membranes modified with polyethyleneimine for elucidating enhanced monovalent permselectivity of electro dialysis**

Wenbin Jiang (New Mexico State University)\*, Lu Lin (New Mexico State University), Xuesong Xu (New Mexico State University), Pei Xu (New Mexico State University)

Monovalent permselective cation-exchange membrane (CEM) CR671 was developed by coating polyethyleneimine onto the normal grade CEM CR67. Pilot-scale electro dialysis of brackish groundwater demonstrated excellent monovalent permselectivity of the CR671 as compared to the CR67. Advanced analytical approaches were employed to characterize the physicochemical and electrochemical properties of the CEMs to elucidate the mechanisms of permselectivity. Ion-exchange capacities of the CR671 and CR67 were measured to be 2.0 and 2.1 meq/g dry membrane, respectively. Zeta-potential analysis revealed that the CR671 surface was positively charged as a result of polyethyleneimine coating. Electrochemical impedance spectroscopy (EIS) data indicated larger impedance for the CR671 and fitted well to the Maxwell-Wagner model, which provided an equivalent electric circuit for the CEMs, as well as indication of the existence of polyethyleneimine layer. The time constants of different ions transporting through polyethyleneimine modification layer were calculated based on the EIS responses. The results revealed the polyethyleneimine modification layer led to longer transport time for Ca<sup>2+</sup> ions through the CR671 than for Na<sup>+</sup> ions, supporting the pilot-scale testing results that the CR671 improved the Na<sup>+</sup> removal by selectively rejecting Ca<sup>2+</sup> ions. However, the difference in ion transport time became less significant with increasing ionic strength of the feed water. The EIS results suggest the monovalent permselectivity decreased during treatment of higher salinity water, supporting the finding that the CR671 exhibited higher monovalent permselectivity during electro dialysis of brackish groundwater than reverse osmosis concentrate in which the salt concentration was 5.7 times higher than the brackish groundwater. The study demonstrates that ion transport time constant is a better indicator for permselectivity of modified ion-exchange membranes than electrical resistance measured by EIS.

**WEDNESDAY 11:30 am** - Kings Garden 5

**27e - Unraveling the Film-Formation Kinetics during Interfacial Polymerization via Low Coherence Interferometry**

Xin Liu (Southern University of Science and Technology)\*, Weiyi Li (Southern University of Science and Technology), Zhuo Li (Southern University of Science and Technology), Anthony Fane (Singapore Membrane Technology Centre), Baolin Deng (Southern University of Science and Technology)

Interfacial polymerization (IP) is one of the most important methods for fabricating thin film composite (TFC) membranes. Understanding the underlying mechanisms of the IP-film formation is of great value for the development of membranes with enhanced performance. The current work employed a novel method to in-situ characterize the film-formation kinetics. This method exploited low coherence interferometry (LCI) to in-situ measure the variation in the optical properties at the interface where polymerization was induced by bringing together two monomers (1,3,5-benzenetricarbonyl trichloride, TMC 0.15 wt% in hexane, and m-phenylenediamine, MPD 2 wt% soaked in the polysulfone substrate membrane). A numerical algorithm was developed to mitigate the effects of the perturbed interface and therefore enabled the surface-averaged intensity (SAI) profiles to resolve different kinetic regimes. To the best of our knowledge, this is the first demonstration of applying LCI to the characterization of an IP process. All the characterization results not only confirm the theoretical model but also provide direct evidence for the different polymerization processes at varied depths (i.e., the asymmetric growth of the IP film).

**WEDNESDAY 12:00 pm** - Kings Garden 5

**27f - Operando Membrane Spectroscopy for Elucidating Transport Mechanisms in Membranes**

Casey O'Brien (University of Notre Dame)\*

Operando spectroscopy is a technique that is commonly used in catalysis to elucidate catalytic reaction mechanisms. It involves the spectroscopic characterization of the catalytic material coupled with simultaneous measurement of catalytic reaction rates under realistic reaction conditions. By characterizing the structure of the catalyst and measuring reaction rates simultaneously, one can obtain detailed structure-function relationships and elucidate reaction mechanisms in more detail than is possible with ex-situ characterization techniques. While operando spectroscopy has been used almost exclusively to study catalytic materials, other fields such as gas separation membranes would benefit from the operando spectroscopy tools and techniques. Towards this end, our research group has dedicated the last three years to developing operando spectroscopy tools for elucidating transport mechanisms in gas separation membranes. In this talk, I will discuss our results with two types of gas separation membranes: (1) Pd-based H<sub>2</sub> separation membranes, and (2) PVAm facilitated transport membranes. Pd-based membranes are attractive for H<sub>2</sub> separation applications, however, other gases that are common to H<sub>2</sub>-containing gas streams, such as CO, C<sub>3</sub>H<sub>6</sub>, and H<sub>2</sub>S, can severely inhibit hydrogen transport. The fundamental mechanisms by which these gases inhibit hydrogen transport is not well understood. To address this problem we have developed an operando spectroscopy tool that can monitor the reactions occurring on the surface of Pd-based membranes using polarization-modulation infrared reflection absorption spectroscopy and simultaneously measure hydrogen permeation rates. I will demonstrate that this tool can elucidate unknown poisoning mechanisms in great detail. We have also developed an operando spectroscopy tool for elucidating CO<sub>2</sub> transport mechanisms in PVAm FTMs using transmission FTIR spectroscopy.

**WEDNESDAY 12:00 pm** - Ballroom 3

**28a - Biofouling resistant membranes for wound healing**

Antoine Venault (Chung Yuan Christian University)\*, Hao-Tung Lin (Chung Yuan Christian University), Yung Chang (Chung Yuan Christian University)

Low-biofouling porous membranes are widely applied to wastewater treatment, but their inherent properties make them ideal potential candidates for a totally different use: wound healing. An ideal wound dressing should maintain a moist environment above the wound. Besides, it should be highly porous to promote gas exchanges and exudates drainage, resistant to bacterial attachment to prevent wound infection and more generally resist to the attachment of proteins and cells (so called non-sticky property) to avoid secondary injuries following dressing removal/change. Low-biofouling porous membranes meet all of these requirements. We have applied different surface modifications to polytetrafluoroethylene membranes using PEGylated, zwitterionic or pseudo-zwitterionic materials, and studied their ability to resist biofouling by proteins, blood cells, bacteria or fibroblast cells. Then, applied as bandages onto wounds on model rats, we observed significant improvement of wound healing kinetic/quality, as compared with wounds covered with commercially available bandages. Parallely, we worked with chitosan soft-membranes and enhanced the biocompatibility of the natural polymer via a proper surface modification starring a copolymer of glycidyl methacrylate units and sulfobetaine methacrylate moieties. We applied the grafted chitosan in the healing of diabetic wounds. This work was supported by the Ministry of Science and Technology of Taiwan (project grant MOST 108-2923-E-033 -001)

**WEDNESDAY 2:30 pm** - Ballroom 4**28b - Impacts of Bio-inspired Zwitterionic Membranes for Health Care Applications**, Yung Chang (R&D Center for Membrane Technology, CYCU)\*

Bio-inspired zwitterionic materials are the latest generation of biomaterials for nonfouling interfaces and membranes in health care applications. This talk summarizes our fundamental developments in R&D Center for Membrane Technology (Taiwan) related to the functionalization of interfaces and membranes using zwitterionic materials. Our molecular designs of zwitterionic polymers and copolymers, sulfobetaine-based, carboxybetaine-based, or phosphobetaine-based, will be reviewed. Then, the strategies used to functionalize surfaces/membranes by coating, grafting onto, grafting from, or in situ modification will be introduced, and the important part of this talk will be the focus to key medical applications of zwitterionic membranes. Finally, some potential future directions for molecular designs, functionalization processes, and applications will be summarized. This work was supported by Ministry of Science and Technology in Taiwan. (MOST 108-2923-E-033 -001) References [1] C. C. Lien, L. C. Yeh, A. Venault, S. C. Tsai, C. H. Hsu, G. V. Dizon, Y. T. Huang, A. Higuchi and Y. Chang, *Journal of Membrane Science*, 565, 119-130 (2018). [2] Y. W. Chen, A. Venault, J. F. Jhong, H. T. Ho, Y. Chang, *Journal of Membrane Science*, 537, 355-369 (2017). [3] A. Venault, K. M. Trinh, Y. Chang, *Journal of Membrane Science*, 501, 68-78 (2016). [4] A. Venault, M. R. B. Ballad, Y. H. Liu, P. Aimar, Y. Chang, *Journal of Membrane Science*, 477, 101-114 (2015). [5] S. H. Chen, Y. Chang, K. R. Lee, J. Y. Lai, *Journal of Membrane Science*, 450, 224-234 (2014). [6] A. Venault, Y. Chang, H. H. Hsu, J. F. Jhong, J. Huang, *Journal of Membrane Science*, 439, 48-57 (2013).

**WEDNESDAY 3:00 pm** - Ballroom 4**28c - Biomimetic membrane systems utilizing electro-dynamic interfaces**

Bruce Hinds (University of Washington)\*

An important challenge for the membrane community is to mimic 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. CNT membranes, 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. Use of the electro-osmotic phenomenon for responsive/programmed transdermal drug delivery devices for nicotine addiction. Electrophoresis and electroosmosis phenomena are discussed in detail through CNT conduits. 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-NTA 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. The separation efficiency of  $1\text{cm}^2$  of membrane was comparable to convention  $1\text{cm}^3$  volumes used in chromatography. Further modeling of system kinetics shows order of magnitude increase in throughput with sub-second cycle times enabled with high imidazole concentrations in a continuous cross flow operation.

**WEDNESDAY 3:30 pm** - Ballroom 4

**28d - Responsiveness and function of DNA-gated membranes**

Beñat Olave (Polymat, University of the Basque Country), Iliane Rafaniello (Polymat, University of the Basque Country), Thomas Schäfer (Polymat, University of the Basque Country)\*

DNA-aptamers are oligonucleotides that can be designed to specifically interact with a molecular target coinciding with a conformational change. We have previously shown that such DNA-aptamers can function as "gate keepers" in nanoporous membranes where a molecular recognition event modulates membrane permeability. The gating function of the aptamer was proven to be reversible, specific, and target concentration dependent. However, a significant drawback of the system consisted in the necessity of fine-tuning between pore size of the membrane support and the DNA-aptamer dimensions in order to fulfil its gating function. A way to overcome this limitation is taking advantage of the versatility of DNA and create DNA-aptamer sandwich structures which are scalable in size. We monitored the build-up of such structures in real time using quartz crystal microbalance with dissipation measurement and multi-parameter surface plasmon resonance using a multiple wavelength mode. Both techniques allowed quantifying the length-scales of the DNA-sandwich created and, in this way, optimize systematically the design of the responsive membrane. The resulting responsive DNA-nanostructure was widely independent of the pore size of the membrane support and the flexibility of the DNA-based responsive membrane was significantly increased. We investigated the responsiveness and thermodynamic basics of the DNA-gating in more detail. Attention was focused on whether there exists a trade-off between membrane stability and break-up upon target recognition. We studied in how far a change in sensitivity of the DNA-aptamer occurred when incorporated in a sandwich structure. We found that creating responsive DNA-nanostructures based on aptamers is not as straightforward as can be found reported in literature. However, the versatility of the DNA-building blocks offer ample possibilities for optimisation, strategies for which will be critically discussed.

**WEDNESDAY 4:00 pm** - Ballroom 4

**28e - Nature-inspired Coating-free Membranes for Desalination**

Himanshu Mishra (King Abdullah University of Science and Technology), Ratul Das ( King Abdullah University of Science and Technology), Sankara Arunachalam (King Abdullah University of Science and Technology), Zain Ahmad (King Abdullah University of Science and Technology), Edelberto Manalastas (King Abdullah University of Science and Technology), Jamilya Nauruzbayeva (King Abdullah University of Science and Technology)\*

Membrane distillation (MD) processes typically utilize membranes with perfluorinated coatings to extract pure water vapor from hot saline feeds. This choice of chemicals is based on the conventional wisdom that water-repellent coatings prevent the intrusion of water due to capillary forces. However, the time-dependent loss of wetting of those coatings due to the deposition of amphiphilic foulants and/or coating-damage under high operational temperatures or abrasion is limiting their scope. Thus, coating-free membranes that could prevent liquid intrusion are desirable, but they have remained unachievable with intrinsically wetting materials so far. Here, we report on the development of biomimetic coating-free gas-entrapping membranes (GEMs) inspired by the cuticles of springtails and hairs of *Halobates germanus*, both of which exhibit mushroom-shaped features. We demonstrate that, against common expectation, intrinsically wetting materials can reliably prevent the intrusion of liquids after carving those biomimetic microtextures onto them; the solid-liquid-vapor system is trapped into metastable Cassie-states whose life-time could be tuned by the shape and size of the pores. We used silica and poly(methyl methacrylate) (PMMA) as model systems to realize GEMs by carving arrays of microscale cylindrical pores with mushroom-shaped inlets and outlets. Remarkably, both silica- and PMMA-GEMs robustly entrapped air in upon immersion in water at 293 K and 1 atm, which stayed intact in the pores for over six weeks. When our PMMA-GEMs (porosity,  $\phi=0.1$ ) were used to separate a solution of  $\sim 0.6$  M NaCl at 333 K from deionized water at 288 K, the vapor flux of the desalinated water was  $J \sim 1$  L-m<sup>-2</sup>-h<sup>-1</sup>. To our knowledge, this is the first demonstration of coating-free desalination by MD. Our bio-inspired strategy might advance the rational design of coating-free membranes, from common materials, exhibiting superior resilience against higher temperatures and fouling.

**WEDNESDAY 4:30 pm** - Ballroom 4

**28f - Carbon nanotube porins as model biomimetic membrane nanopores**

Aleksandr Noy (Lawrence Livermore National Laboratory)\*

Controlling ion and water transport on a molecular scale is fundamental for membrane applications ranging from industrial water treatment, to chemical separations, to advanced batteries and fuel cells. Living systems move ions and small molecules across biological membranes using protein pores that rely on nanoscale confinement effects to achieve efficient and exquisitely-selective transport. I will show that carbon nanotube porins-pore channels formed by ultra-short carbon nanotubes assembled in a lipid membrane-can exploit similar physical principles to transport water, protons, and small ions with efficiency that rivals and sometimes exceeds that of biological channels. I will discuss the role of molecular confinement and slip flow in these pores and show how it can enhance water and proton transport efficiency and influence the mechanisms of ion selectivity in these pores. Overall, carbon nanotube porins represent simple and versatile biomimetic membrane pores that are ideal for studying nanoscale transport phenomena and building the next generation of separation technologies.

**WEDNESDAY 2:00 pm** - Kings Garden 5

**29a - A novel method to distinguish between crystal and defect transport in zeolite membranes**

David Carter (University of Ottawa), Shaaima Al Akwa (University of Ottawa), Boguslaw Kruczek (University of Ottawa)\*, Handan Tezel (University of Ottawa)

Zeolite-based inorganic membranes have an extraordinary potential to separate gas mixtures at modest temperatures and pressures. However, this potential has not yet been realized, in part because of difficulty in forming a continuous, defect-free layer of zeolite crystals. The presence of defects in zeolite membranes arises from, for example, incomplete zeolite crystal growth and thermally induced linear expansion differences between zeolite crystals and the membrane support. The presence of defects is manifested by a decrease in membrane selectivity; however, the selectivity of the zeolite membrane alone does not allow quantitative determination of defect characteristics, without which any attempts to improve membrane synthesis protocols are highly empirical. In this paper we present a novel method that distinguishes between the crystal and defect transport of gases in zeolite membranes. The proposed method relies on single gas permeation tests with He and N<sub>2</sub> before and after calcination of the membrane, and knowledge of the adsorption isotherms of these gases on the zeolite crystals incorporated into the membrane. The validity of the method is verified by comparing the experimental and predicted permeances of He and N<sub>2</sub> before and after membrane calcination at different feed pressures. In addition, knowing the surface diffusion coefficient ratios from literature of N<sub>2</sub> with other adsorbing gases, for example CO<sub>2</sub> and CH<sub>4</sub>, the proposed method allows prediction of membrane permeances of these gases. These permeances can then be compared with the experimental data, thus serving as another verification for the method. The application of the proposed method is demonstrated using silicalite zeolite membranes, prepared by the pore-plugging technique, inside porous TiO<sub>2</sub> supports.

**WEDNESDAY 2:30 pm** - Kings Garden 5

**29b - Study on antifouling behaviors of GO modified nanocomposite membranes through QCMD and surface energetics analysis**

Amin Karkooti (University of Alberta), Neda Nazemifard (University of Alberta), Mohtada Sadrzadeh (University of Alberta)\*

Membrane fouling is the main challenge that limits the practical application of membranes in water reclamation. Development of nanocomposite membranes may provide an effective solution to improve membrane-fouling resistance. Membrane surface properties are significant factors affecting initial membrane fouling, where hydrophilic surfaces are generally less prone to fouling. The extent of adsorption of foulants to the membrane surface depends on membrane-foulant affinity, which relies on the nature of the foulant and membrane material. In the present work, an extended DLVO (aka XDLVO) interaction energy analysis was employed to explain the adsorption of organic foulant to the surface of the ultrafiltration membrane with different degree of hydrophilicity. The fundamental interactions (van der Waals, electrostatic, and acid-base interaction) that control organic fouling were evaluated. In addition, a quartz crystal microbalance with dissipation monitoring (QCM-D) was employed to investigate organic matter adsorption/desorption to/from a thin layer of membranes. The amount of adsorption/desorption and the mass of deposited structures on membranes were measured by real-time monitoring of resonance frequency and energy dissipation changes ( $\Delta f$  and  $\Delta D$ ). To obtain different hydrophilicity of membranes, graphene oxide (GO) nanosheets and polyvinylpyrrolidone (PVP) were added into the polyethersulfone (PES) casting solution. Finally, in order to validate the XDLVO and QCM-D results the surface properties of the membranes were characterized by contact angle analyzer, fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), zeta potential measurement, and flux recovery ratio (FRR) tests. The information on membrane-foulant interaction is critical to optimize use of additives and to reduce the membrane fouling.

**WEDNESDAY 3:00 pm** - Kings Garden 5

**29c - 3D characterization of polyamide reverse osmosis membranes**

Tyler E Culp (Penn State University)\*, Manish Kumar (Penn State University), Enrique Gomez (Penn State University)

Polyamide-based thin-film composite membranes used for reverse osmosis (RO) are at the forefront of water desalination and purification technologies due to their high salt rejection, high energy efficiency, and ease of operation. Nevertheless, in spite of the benefits of RO membranes, many open questions about the internal nanostructure of the membrane active layer remain, such as the distribution of voids, surface area and mass. We demonstrate that with transmission electron microscopy, where electron tomography is used to obtain a three-dimensional (3D) reconstruction of the polyamide active layer, these parameters can be quantified to a series of RO membranes. The application of quantitative 3D characterization tools provides a strategy for linking the morphology to water transport properties of RO membranes.

**WEDNESDAY 3:30 pm** - Kings Garden 5

**29d - Selective Ion Transport Properties of Membrane Materials**

Anita Hill (CSIRO)\*, Aaron Thornton (CSIRO), Cara Doherty (CSIRO)

Closed loop material reuse and recycling is enabled by separations technology. Mechanisms to separate ions and molecules rapidly, efficiently, and with high purity are achievable; however, currently these methods are found only in nature. Progress in fast selective molecular transport within membranes has been achieved via free volume elements with characteristics, such as those found in zeolites of well-defined cavity and neck topologies, that allow multiple wide pathways for flow connected by smaller sieving pathways. These topologies mimic those of biological membrane channels. The fundamental principles underlying fast selective transport in biological channels originate in the architecture of the pore. Advances in materials chemistry and characterization have made it possible to produce porosity in synthetic materials that can imitate these biological channels. The need for membrane materials with the ability to perform low energy molecular and ionic separations is increasing as the world transitions to a circular economy. For example, the separation and recovery of critical metals from process streams using low energy membrane technology not only contributes to recycling but also provides resiliency in the face of national shortages of these critical metals. We examine free volume elements, as measured by positron annihilation lifetime spectroscopy, in a range of materials that enable outstanding molecular and ionic transport and separation performance.

**WEDNESDAY 4:00 pm** - Kings Garden 5

**29e - Membrane-based oil-gas separation for dissolved gas-in-oil extraction: gas transport properties of ceramic supported Teflon membranes**

Liang-Chih Ma (Arizona State University)\*, Chuan Chen (Global Energy Interconnection Research Institute Co., Ltd.), Jerry Lin (Arizona State University)

Dissolved gas extraction from transformer oil is an indispensable part in dissolved gas analysis (DGA) for transformer fault monitoring and diagnosis. Membrane-based oil-gas separation represents a promising approach for dissolved gas-in-oil extraction in terms of operation and maintenance, long-term stability, and cost competitiveness. However, no comprehensive study available in the literature on gas transport properties of membranes during the oil-gas separation process. Therefore, the objective of the present study is to clarify gas transport properties of our developed Teflon AF2400/ceramic composite membranes during the oil-gas separation process, focusing on both kinetics and thermodynamics aspects. In the study, effects of operating temperature, oil feed flow rate as well as stirring rate on the equilibrium time and the equilibrium level for 7 characteristic gases (i.e. H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub>) have been investigated. The gas-dissolved oil used for oil-gas separation experiments was prepared by the standard mixed gas which comprises 7 characteristic gases with 5,000 ppmv balanced with Ar. The results show that the rate-limiting step in the oil-gas separation process is gas diffusion through the oil instead of the membranes. Reduced equilibrium time can be achieved by increasing oil feed flow rate and/or stirring rate due to enhanced gas diffusivity in the oil. In addition, it was found that the driving force for gas permeation is the gas concentration difference between the oil and the permeate side at 1 atm and thus the equilibrium time strongly depends on the Henry's law solubility constant. Except H<sub>2</sub>, since the solubility constant decreases with increasing temperature, the equilibrium time would decrease with increasing temperature even though the gas diffusivity in the oil increases. Finally, the equilibrium level, which is determined by the solubility constant, cannot reach 100% due to the driving force limited in the dilute system.

**WEDNESDAY 4:30 pm** - Kings Garden 5

**29f - Porous support of TFC membranes: Does it truly have negligible resistance?**

Masoud Aghajani (University of Colorado Boulder)\*, Alan R. Greenberg (University of Colorado Boulder), Yifu Ding (University of Colorado Boulder)

For thin film composite (TFC) membranes, the polyamide barrier layer is generally believed to be responsible for the entire resistance to water permeation, while the resistance of the porous support is considered as negligible. However, this understanding is based on the "separate" rating of the resistance of the porous support under high trans-membrane pressure (TMP), which is distinctively different from the situation during high-pressure reverse osmosis (RO). Specifically, during RO, the porous support is under much higher mechanical loading (the overall TMP of the TFC membrane) but a significantly lower permeation rate (low TMP across the support). Such high mechanical loading, e.g. 7 MPa (>1000 psi) during seawater desalination is above the yield strength of the porous support and can cause substantial mechanical deformation, especially over an extended period of time. To measure the true resistance of the porous support during high-pressure RO, we developed a new measurement method that uses a series arrangement of a TFC membrane on top of a typical porous support. Our results show that, under high overall TMP (> 5 MPa), the plastic deformation of the additional porous support is as much as 3X larger than that of the same support subjected to identical TMP but without the TFC membrane on top. A direct relationship is observed between the applied TMP and the plastic deformation of the porous supports. Moreover, DI water permeation experiments revealed an order of magnitude increase in resistance for the deformed porous supports in comparison to the pristine (undeformed) ones. Most importantly, our analysis indicates that the resistance of a representative commercial porous support used to fabricate TFC membranes can account for up to 33% of the overall TFC membrane resistance during high pressure permeation (5.5-8.2 MPa).

**WEDNESDAY 2:00 pm** - Kings Garden 4

**30a - Numerical and experimental studies on the deposition of sticky particles near a membrane surface**

Seon Yeop Jung (Seoul National University)\*, Kyung Hyun Ahn (Seoul National University)

Deposition of sticky particles onto a membrane surface is studied by numerical simulation and experiment. During a membrane separation process, which is a core unit operation in water purification, bioprocessing, or pharmaceutical manufacturing, particle deposition and cake layer formation are induced by the continuous accumulation of rejected matters onto the membrane surface. Although deposition of particles is affected by complex interactions such as hydrodynamic, particle-particle, and particle-membrane interactions, comprehensive modeling and simulation of particle deposition dealing with those interactions have rarely been conducted. In addition, a prescribed velocity field was often assumed in the majority of previous studies which neglected the influence of particle cake layer onto the surrounding flow behavior. In this study, we propose a simple algorithm to roughly capture the interplay between cake layer formation and flow structure in the implementation of a modified Brownian Dynamics (BD) simulation, which tracks floating particles exerted by various forces. A surface spring was introduced in our simulation to model complex attractive interactions between particles. We defined a dimensionless number named  $S$ , defined by the ratio of the attractive force by the surface spring to the Stokes' drag force near a membrane surface, to manipulate the extent of attractive forces. A distorted flow field was generated near a particle cluster and it affected the progress of particle deposition. We compared the configuration of deposited particles with and without this new algorithm for the credible reproduction of particle deposition phenomenon. A microfluidic experiment with microalgae was conducted to capture the particle deposition and cake layer formation onto a surface of a constructed porous region. A qualitative agreement with the numerical simulation and experiment was identified in the growth of the cake layer and local movement of floating particles.

**WEDNESDAY 2:30 pm** - Kings Garden 4

**30b - Characterization of the Striping Phenomenon during Membrane Fouling via Optical Coherence Tomography**

Weiyi Li (Southern University of Science and Technology)\*, Xin Liu (Southern University of Science and Technology), Anthony Fane (Singapore Membrane Technology Centre)

Mitigating membrane fouling entails powerful tools to study the complex transport phenomena occurring in the polarized boundary layer and thereby provide deeper insights into the development of a fouling layer. The current study employed a novel method to in-situ characterize a fouling process during ultrafiltration. This characterization method was based on an advanced optical technique, that is, optical coherence tomography (OCT). The focus of the current study was to dynamically capture the formation of 'stripes', which are dissipative structures in the boundary layer discovered about 30 years ago but attracted little attention in the field of membrane separations. Various algorithms were developed to analyze the OCT datasets and generate a series of digitalized fouling layers for resolving the evolution of the fouling layer on a micron scale. It was revealed that the striping phenomenon should play an important role during both the initial and long term fouling; the vortices induced by the wall permeation could be a critical mechanism accounting for the deposition and removal of the foulants at the liquid-membrane interface. Useful implications were obtained for the system design to intensify the secondary flows in the boundary layer and thereby alleviate the membrane fouling.

**WEDNESDAY 3:00 pm** - Kings Garden 4

**30c - A closer look at biofouling: time-lapse optical microscopy of biofilm formation in wastewater reuse**

Emily W Tow (Olin College)\*, Behzad Rad (Lawrence Berkeley National Laboratory), Robert Kostecki (Lawrence Berkeley National Laboratory)

Biofouling is commonplace in wastewater reuse, but we rarely get the chance to see inside the slime. Biofilms tend to form on the microfiltration and reverse osmosis membranes utilized in advanced treatment of wastewater due to its high organic and microbial content. Biofouling raises the cost of water reuse by necessitating frequent membrane cleaning and, in some cases, irreversibly damaging membranes. Although cost-effective fouling mitigation requires understanding of biofilm behavior in wastewater reuse, existing biofilm visualization research focuses on other applications. Therefore, in this study, we use confocal microscopy to capture time-lapse images of biofouling on wastewater reuse membranes. Secondary effluent from municipal wastewater treatment (prior to disinfection) obtained from California's East Bay Municipal Utility District was used as the feedwater. It was stained using fluorescent wheat germ agglutinin to label extracellular substances as well as Hoechst 33342 and propidium iodide probes to differentiate live from dead cells. A miniature cross-flow membrane cell was created to operate microfiltration and ultrafiltration and at typical flow rates and transmembrane fluxes, with and without periodic backwashing, for periods of 1-5 days. Meanwhile, the biofilms that formed on the membranes were imaged in situ with a confocal laser scanning microscope. Imaging was also conducted during several clean-in-place procedures. Although single-cell resolution was attained in some images, larger maps were also obtained to observe heterogeneity on the millimeter scale. Images demonstrate biofilm accumulation and removal mechanisms including cell proliferation and EPS production as well as film detachment, wrinkling, sloughing and re-deposition. These images provide insight into biofilm behaviors specific to wastewater reuse and inform the development of targeted biofouling mitigation strategies.

**WEDNESDAY 3:30 pm** - Kings Garden 4

**30d - Improved graphene oxide membrane increases membrane distillation desalination of RO concentrate**

Samuel Olatunji (Texas A&M University-Kingsville), Lucy M Camacho (Texas A&M University-Kingsville)\*

Commercialization of membrane distillation (MD) as a feasible alternative for desalination is limited due to the inexistence of membranes specifically designed to meet the needs of the MD desalination process. The ideal properties of a MD membrane are fundamentally different from those of reverse osmosis (RO). The main difference is based on the hydrophobicity of the MD membrane. In this research, a dry-wet phase inversion method was used to synthesize an optimal graphene oxide (GO) membrane that is suitable for MD desalination. The effect of pH of the GO sheets used as source material for the GO membrane was also evaluated. SEM studies showed that the hydrophobic properties of the synthesized GO membrane varies with the dry-wet phase inversion method as compared to the method of dry- or wet-phase inversion. The pH of the GO sheets also plays a critical role on the properties of the membrane. The new GO membrane was tested with simulated and real brackish RO concentrate in a portable pilot MD system. It was found that the new membrane can produce a permeate flux of 85 L/m<sup>2</sup>·h, which is higher than the flux produced by a commercial polypropylene (PP) membrane tested with MD under the same operational conditions. The results indicated that the GO membrane prepared with the wet-dry phase inversion method increases the water recovery of the RO system by more than 98%. The MD process using the proposed synthesized GO membrane shows promising water recovery, salt rejection, and brine reduction from brackish RO concentrate.

**WEDNESDAY 4:00 pm** - Kings Garden 4

**30e - Automated real-time membrane biofouling assessment using microbial enzyme activity**

Babar K Khan (King Abdullah University of Science and Technology)\*, Luca Fortunato (King Abdullah University of Science and Technology), TorOve Leiknes (King Abdullah University of Science and Technology)

The advent of advanced membranes for water desalination over the past several decades have greatly improved water purification processes. Biofouling is a major recurring cost driver for membranes used in desalination and play a major role in membrane life-cycle assessment. A number of methods have been developed to detect bacterial growth and provide cleaning guidance, but most suffer from either being unviable in-situ or are not capable of early biological detection. An automated at-line sensor was devised and operated with real seawater to measure biofouling over time in NF and RO membrane modules. The system samples the membrane module in-situ by injecting artificial fluorogen bound to substrate (fluorogen-substrates) at discrete time points and measures fluorescence from the liberated fluorogen in real-time. The signal has been correlated to microbial extracellular enzyme activity. Our results demonstrate the capability to track microbial biomass from initiation of colonization to biofouling on the membrane surface. This approach has the advantage of indirectly measuring bacterial abundance on membranes not readily adaptable for direct visualization (RO membrane modules), without the need for sophisticated techniques found in other molecular approaches (ATP). Our results indicate that fluorogen-substrate cleavage can be used in early biofouling detection as a prognostic tool to guide cleaning protocols for membranes in aqueous systems. In this study, fluorogen-substrate cleavage by bacterial extracellular enzymes was used to monitor microbial colonization proximal to the surface of membrane filtration systems non-invasively using an automated system. Biofouling is a major impediment to the lifecycle of membranes, therefore measuring enzymatic activity by fluorogen-substrates cleavage can be utilized to monitor membrane health for guiding anti-biofouling practices, enabling both assessment, targeted cleaning, and therefore extension of the membrane lifespan.

**WEDNESDAY 4:30 pm** - Kings Garden 4

**30f - Interactions between extracellular polymeric substances and zwitterionic hydrogels as a designing tool for antifouling surfaces**

Angelin Ida Vedhamanickam (Ben-Gurion University of the Negev)\*, Nir Goldberg (Ben-Gurion University of the Negev), Ronit Bitton (Ben-Gurion University of the Negev), Moshe Herzberg (Ben-Gurion University of the Negev)

Membrane fouling by microbial biofilm components, mainly extracellular polymeric substances (EPS) is a major impediment of the membrane filtration process, which can significantly reduce membrane performance. Common promising approach for biofouling mitigation focuses on reducing adsorption of EPS to membrane surface by surface modification using zwitterionic polymers. However, favorable interactions between the EPS and the hydrogel coating, in our case poly-sulfobetaine (poly-SPE), will reduce the coating anti-fouling efficiency. Currently, the common design of hydrogel-coated membranes with poly-zwitterions is based on "trial and error" approach in a sense of analyzing membrane performance during filtration tests of different fouling and biofouling agents, for a certain coating condition. The overall aim of the proposed research is to utilize a detailed characterization of the poly-zwitterions (poly-SPE in our case), EPS components and interactions between them, on the surface and in solution, as a tool to tailor better performance of the anti-fouling, hydrogel-coated membranes. The effects of EPS model compounds on the polySPE in solution (bulk-physical properties) using small angle x-ray scattering (SAXS) were compared to adsorption experiments of the EPS model compounds to pristine and modified polysulfone (PSF)-coated sensors of quartz crystal microbalance with dissipation monitoring (QCM-D). The positive correlation between the SAXS and QCM-D results, in which fruitful interactions were observed, indicating interactions in solution can be used as a tool to predict interaction of foulants and the protective polySPE layer, under variety of aquatic conditions. At last, the predicted successes and limitations of the well characterized polySPE protective layer were confirmed by fouling experiments of pristine and modified ultrafiltration (UF) membranes.

**WEDNESDAY 2:00 pm** - Kings Garden 3

**31a - Optimizing Microfluidic Nanoparticle Capture from Biofluids on Ultrathin Silicon Nanomembranes: A Computational and Experimental Analysis of Tangential Flow Analyte Capture (TFAC)**

Kilean Lucas (University of Rochester)\*, Danial Ahmad (University of Rochester), Mehdi (Aslan) Dehghani (Rochester Institute of Technology), Thomas Gaborski (Rochester Institute of Technology), Richard Waugh (University of Rochester), James McGrath (University of Rochester)

Extracellular vesicles (EVs) are lipid vesicles ranging from 30 - 1000 nm in diameter secreted by cells to serve a variety of functions. Certain members of the EV family, such as exosomes, are thought to be important for intercellular communication. Exosomes contain cell specific biomarkers (i.e. miRNA, protein) that are useful for point-of-care (POC) diagnostics. A variety of techniques are used to isolate EVs, including ultracentrifugation, affinity-based capture, precipitation and filtration, but these often require large sample volumes (50 - 300 mL) which are not feasible for a POC system. Additionally, these isolations are often contaminated with protein, leading to difficulty in the identification of biomarkers. Therefore, an alternative method of isolating EVs from small volumes is required for POC. Silicon nanomembranes are ultrathin (50-100 nm) nanoporous membranes discovered during the rapid crystallization of pure silicon films. These membranes are manufactured with a variety of pore diameters (~ 5 nm - 100 nm) and have high porosities (20% - 40%) and exceptional permeabilities. These membranes are manufactured in a 'chip' format that is 5.4 mm x 5.4 mm, making them perfect for small volume applications such as microfluidic filtration. In this work, we present a novel exosome capture method for small volume (~ 1 mL) samples. We call this method tangential flow analyte capture (TFAC). After demonstrating the capture of exosomes from undiluted serum, we present a computational model for TFAC that is validated with 60 nm gold nanoparticles with and without the addition of serum albumin (2 mg/ml). We use the model to define optimal capture conditions, and then demonstrate the capture of > 75% of exosomes from defined protein/exosome sample and compare these results to capture from raw urine.

**WEDNESDAY 2:30 pm** - Kings Garden 3

**31b - Development and scale-up of laterally-fed membrane chromatography for the purification of therapeutic viruses**

Karina Kawka (McMaster University)\*, Pedram Madadkar (McMaster University), Shabnam Shoaebargh (McMaster University), Natasha Kazhdan (McMaster University), Maria Fe C. Medina (McMaster University), Brian Lichty (McMaster University), Raja Ghosh (McMaster University), David Latulippe (McMaster University)

Viruses are a new class of biotherapeutics with potential to treat a number of diseases including cancer and there exists a number of different types depending on the application. While adenoviruses are the most used type in gene therapy, rhabdoviruses have potent oncolytic (cancer-killing) activity and are currently under clinical trials in Canada. Limitations with respect to large-scale virus purification (i.e. removal of host-cell proteins and DNA) are one of the major obstacles between these therapeutics and patients. Although membrane chromatography has great potential to address this issue, the radial-flow configuration most commercial MC devices are currently designed causes non-uniform flow distribution, affecting the performance of the separation. Our group has demonstrated the advantages of the laterally-fed membrane chromatography (LFMC) over radial flow MC, which include lower sample dilution and higher virus purities when 5 mL of adenovirus culture were purified using 1 mL devices (i.e. membrane volume). Recent scale-up experiments with 50 to 100 mL of adenovirus culture using the Sartobind Q anion-exchange membrane and 1 mL LFMC devices resulted in virus recoveries close to 100% and removal of contaminant proteins and DNA reaching 90%. However, only 40% recovery was obtained when 200 mL of culture was processed because the binding capacity of the membrane was exceeded. For this reason, a 10 mL LFMC device was developed to target the purification of up to 1 L of adenovirus culture. As a second objective, the LFMC at 1 mL scale was investigated for the purification of rhabdoviruses. Early results indicate less than 10% virus recovery using the same conditions previously applied for adenoviruses. Even after adjustment of pH and elution conditions, no significant improvement was observed. Therefore, other types of membrane adsorbers based on hydrophobic and pseudo-affinity interactions were tested to maximize rhabdovirus recovery and purity.

**WEDNESDAY 3:00 pm** - Kings Garden 3

**31c - Characterization of EV Secretion at Single Cell Resolution**

Gerardo Mauleon Ramos (University of Chicago)\*, Kilean Lucas (University of Rochester), Vladimir Riazanski (University of Chicago), James McGrath (University of Rochester), Deborah Nelson (University of Chicago)

Extracellular vesicles (EVs) are lipid bilayer enclosed nanocarriers secreted by cells. They are a heterogeneous group of particles generally divided into exosomes, microvesicles or apoptotic bodies depending on their cellular origin, dimension, and tetraspanin surface expression. Circulating EVs carry transmembrane proteins and luminal cargo including soluble cytoplasmic proteins and nucleic acids to other cells. The actual mechanism by which EVs deliver their cargo is still unknown, but, EV cargo is believed to mediate transfer of biologically active molecules between cells. As such, EVs have gained attention as a player in therapeutic delivery. Before EVs can take this step, information on size, concentration of secreted EVs, heterogeneity, and the overall factors that control EV release from secretory cells must be resolved. To investigate these unknown factors, we developed an isolation protocol that allows us to study EV secretion from single cells as a response to a chemical stimulus. Our initial assay uses a novel microfluidic platform that was engineered specifically to allow the measurement of released EVs by cultured cells. Additionally, we are using a filtration based approach to selectively capture secreted EVs based on their size using a novel ultrathin (50nm thick) nanoporous silicon nitride membrane. In order to differentiate between EVs with an intracellular origin from shedding vesicles, we express a fluorescently labelled PI(3,5)P2-specific probe which localizes to the multivesicular bodies and lysosomes. We have deployed this system to establish optimal conditions for EV secretion. Using this combined assay, we have established that the EV population shows at least a 3:1 ratio of membrane shedding vesicles versus exosomes. Additionally, we should be able to use this platform to design screening strategies exploring some of the unknown factors in stimulus-secretion coupling in EV release; size, concentration, secretion dynamics and heterogeneity.

**WEDNESDAY 3:30 pm** - Kings Garden 3

**31d - Charge, size distribution and hydrophobicity of viruses: Effect of the virus purification method**

Hang Shi (Michigan State University), Vlad Tarabara (Michigan State University)\*

Viruses propagated and purified by different methods may exhibit different adsorption, aggregation and electrokinetic behaviors. The differences are caused by residual impurities, either in the dissolved phase or associated with virions. The effects of growth and purification protocols on the isoelectric point, surface tension, and hydrophobicity have not been explored and are the focus of the present work. The study comparatively evaluated two virus propagation methods (in broth and on double agar overlay) and three purification procedures (CsCl density gradient centrifugation, PEG precipitation, and centrifugal diafiltration) in terms of their impact on the properties of resulting virus stocks. Agar-propagated MS2 purified by PEG precipitation or centrifugal diafiltration (100 kDa) included large (~ 0.5 µm) aggregates that persisted through multiple cycles of post-filtration with a 0.1 µm pore size membrane. Regardless of the purification method, such interferences were not observed for MS2 propagated in E. coli broth. Accordingly, the degree of bacteriophage purity achievable with each of the three purification methods was compared based on the data for MS2 and P22 propagated in broth. CsCl density gradient centrifugation produced virus suspensions of highest quality. The impurities remaining in the virus suspension after PEG precipitation and centrifugal diafiltration broadened the size distribution and interfered with either electrophoretic mobility measurements or hydrophobicity characterization or both. The impact on the free energy of virus-virus interaction was especially dramatic with P22 bacteriophage appearing hydrophilic in the presence of impurities and hydrophobic in better purified stocks. The trends in measured physicochemical properties were rationalized by considering impurity-coated virions as permeable soft particles. The obtained data were used to rank the purification methods according to six criteria of likely practical relevance.

**WEDNESDAY 4:00 pm** - Kings Garden 3

**31e - Risk Mitigation Strategies for the use of polymeric consumables for manufacturing of Anti-Sense Oligonucleotides**

Anuradha Vaidya (Biogen), Bill Scott (Biogen)\*, Dave Kolwyck (Biogen)

Due to increased demands on throughput efficiencies, single use systems (SUS) have become widely popular in the Biologics manufacturing industry. However, new modalities such as Anti-Sense Oligonucleotides (ASOs) entail the use of non-conventional upstream and downstream manufacturing conditions involving organic solvents and harsh chemical reagents. As a result, these new modalities present a whole new set of challenges with respect to the use of SUS. In some cases, the worst-case testing conditions historically used to assess the chemical compatibility and performance of SUS are milder than the actual manufacturing conditions. In this presentation, we will present data on the specific risks associated with the application of SUS in Anti-Sense Oligonucleotide manufacturing and suitable mitigation strategies based on comprehensive risk assessments, chemical compatibility studies and leachable studies.

**WEDNESDAY 4:30 pm** - Kings Garden 3

**31f - Use of Nanosphere Self-Assembly to Pattern Nanoporous Membranes for the Study of Extracellular Vesicles**

Marcela Mireles (University of Rochester)\*, Cody Soule (Rochester Institute of Technology), Mehdi Dehghani (Rochester Institute of Technology), Thomas Gaborski (Rochester Institute of Technology)

Nanoscale biocomponents naturally released by cells, such as extracellular vesicles (EVs), have recently gained interest due to their therapeutic and diagnostic potential. Purification and labeling techniques as well as commercially available cell culture membranes have been utilized in an effort to directly or indirectly study exosomes and their effects. Nevertheless, improved platforms for the study of exosomes (30 - 150 nm EVs) are still needed. Adequate membranes, for separation and cell culture, require pore sizes to reach into the nanoscale. These pore sizes cannot be achieved through traditional lithographic techniques and commercially available thick nanoporous membranes commonly exhibit low permeability. Here we utilized nanospheres, similar in size and shape to the targeted EVs, as patterning features for the fabrication of freestanding SiO<sub>2</sub> membranes released through a sacrificial ZnO layer and integrated into silicone-based devices. Through filtration of fluorescent polystyrene beads and exosomes we evaluated the size cut-off characteristics of the membranes as well as their potential for selective permeability of exosomes based on size. The membranes presented here achieved pore sizes of 100 or 250 nm and a thickness of 160 or 300 nm, and demonstrated their potential to allow permeability of exosomes while preventing traffic of microvesicles. This selectivity is crucial for filter-based purification as well as for the modulation of EVs exchange in a co-culture set-up. Overall, this work provides a platform for the direct and indirect study of EVs for which interest will continue to grow.

**WEDNESDAY 2:00 pm** - Ballroom 3

**32a - A Holistic Approach to Explore Interfacially Confined Ionomers Designed for Energy Conversion Device**

Shudipto K Dishari (University of Nebraska-Lincoln)\*

Understanding and improvement of ion transport limitations at nanoscale polymer-catalyst interface is critical to design next generation energy conversion and storage devices. In nanoscale confined ionomeric systems, ion conduction is controlled by ionic domain characteristics, mobility and viscoelastic properties of ionomer layer in a complex manner. In this work, we studied four major fluorocarbon and hydrocarbon based fuel cell ionomers with varied backbone and side chain structures under thin film nanoconfinement. We measured proton conductivity values of sub-micron thick, spin-coated, ionomer films on substrates using electrochemical impedance spectroscopy as a function of film thickness and relative humidity. In addition, the viscoelastic properties of the same films were obtained from peak frequencies of the 1st mode of vibration of AFM tips (in contact with the films) using contact resonance atomic force microscopy (CRFM) and subsequent modeling efforts. The ion conductivity and viscoelastic properties were correlated with thin film morphology (transmission electron microscopy (TEM)), and, ionic domain size and spacing (Small angle X-ray scattering (SAXS)). Finally an innovative approach was adopted to probe zone specific ionomer properties in thin films using fluorescence confocal microscopy. Combining all the information helped us to visualize what is happening with fuel cell ionomers (with varied chemical structure) at nanoscale, and, identify the most important parameters controlling interfacial ion conductivity.

**WEDNESDAY 2:30 pm** - Ballroom 3

**32b - Anion Conducting Membranes Based on Poly(norbornene): High Conductivity, Chemical Stability and Fuel Cell Performance >2.5 W/cm<sup>2</sup>**

Mrinmay Mandal (Georgia Institute of Technology)\*, Garrett Huang (Georgia Institute of Technology), Wanting Chen (Georgia Institute of Technology), Paul A Kohl (Georgia Institute of Technology)

Anion-exchange membranes (AEMs) have widespread applications in electrochemical devices. The development of AEMs with long-term alkaline stability and high hydroxide ion conductivity is of current interest. The use of non-precious catalysts, facile reaction kinetics and reduced fuel crossover are some of the AEM benefits compared to proton-exchange membranes. Previous AEM materials have had low ionic conductivity, poor stability at high pH, and high water uptake. A series of tetrablock copolymers containing non-hydrolyzable backbone and long-chain head-group tethers based on vinyl addition and ring-opening metathesis polymerization (ROMP) of norbornenes were synthesized for use in AEM fuel cells and electrolyzers. Control over the free and bound water uptake, and high hydroxide mobility were achieved by creating phase segregation between the polymer blocks. Polymers with very high IEC values (ca. 3.46 meq/g) were cross-linked with N,N,N',N'-Tetramethyl-1,6-hexanediamine (TMHDA) in order to mitigate unwanted water uptake. The membranes with light cross-link density had record high conductivity, 198 mS/cm at 80°C, for a chemically stable AEM. The AEMs had long-term alkaline stability, as demonstrated by <1% conductivity loss in over 1200 h at 80°C. Ultrathin (ca. 10 μm thick) composite membranes were cast using polytetrafluoroethylene reinforcement. The peak power density of a H<sub>2</sub>/O<sub>2</sub>, hydroxide conducting fuel cell was >2.5 W/cm<sup>2</sup> at 70°C.

**WEDNESDAY 3:00 pm** - Ballroom 3

**32c - High Temperature Fuel Cells with Ion-Pair Membranes and Phosphonated Ionomers**

Michael R Hibbs (Sandia National Laboratories)\*, Cy Fujimoto (Sandia National Laboratories), Ehren Baca (Sandia National Laboratories), Albert Lee (Los Alamos National Laboratory), Yu Seung Kim (Los Alamos National Laboratory)

Recently, Los Alamos National Laboratory in collaboration with Sandia National Laboratories developed phosphate-quaternary ammonium ion-pair coordinated proton exchange polymers. These ion-paired polymers can be used in fuel cell membranes and they have very strong interactions between phosphate ions and quaternary ammonium groups. This enhances water tolerance under high temperature and low relative humidity fuel cell operating conditions. The ion-pair coordinated membrane provides good mechanical properties with a substantially low phosphoric acid doping level and allows for the possibility of polymer membrane fuel cells that operate at temperatures above 200°C. Ion-pair coordinated polymers still have a risk that the acid will be partly evaporated at high temperature operating conditions (> 200°C) or be partly leached out, especially within the electrodes where water is produced. Phosphonic acids can be covalently attached to polymers in order to prevent evaporating or leaching. Because of the impossibility of acid evaporation with phosphonated polymers, the proton conductivity of phosphonated polymers increases with temperature until thermal degradation of the polymers occurs. In this project, we are aiming to develop advanced phosphonated ionomers for ion-pair coordinated polymer electrolyte membrane fuel cells to further improve fuel cell performance. Ionomer synthesis and ion-pair membrane fuel cell results will be included in the presentation. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

**WEDNESDAY 3:30 pm** - Ballroom 3

**32d - High temperature, anhydrous proton conducting membranes and micropatterned bipolar membranes for electrochemical energy conversion and storage technologies**

Christopher G Arges (Louisiana State University)\*

This talk primarily focuses on mild temperature (100 to 250°C) proton conductors composed of polycation polymers, typically used as anion exchange membranes, blended with polybenzimidazole (PBI). These moderate temperature membranes are envisioned for fuel cell systems that operates with hydrogen containing carbon monoxide - produced from steam-reformed methane. Evaluating polycation membrane variants alone demonstrated lower proton conductivity when compared to PBI doped with phosphoric acid (H<sub>3</sub>PO<sub>4</sub>). PBI doped with phosphoric acid, on the other hand, was observed to be unstable above 160°C because of H<sub>3</sub>PO<sub>4</sub> boiling and evaporation. Plus, the PBI-H<sub>3</sub>PO<sub>4</sub> membrane loses its acid due to leaching if condensed water is present (i.e., lack of robust operation if the cell drops below 100°C). To overcome these problems, polycation polymers, were blended with polybenzimidazole (PBI) and these membranes routinely showed conductivity values as high as 0.18 S cm<sup>-1</sup> and were stable under dry and wet conditions and with thermal stability up to 250°C. The talk will close with our recent efforts to pattern polymer electrolyte membrane surfaces to make high surface area bipolar junction interfaces. Larger interfacial surface areas in the bipolar junction region are more effective for water splitting. It is envisaged that an acidic anode and alkaline cathode with a bipolar membrane offers a pathway forward for very low platinum loading fuel cells.

**WEDNESDAY 4:00 pm** - Ballroom 3

**32e - Membrane through-plane alignment of ion-conducting channels**

Xin Liu (Tianjin University), Yi Li (Tianjin University), Jiandang Xue (Tianjin University), Weikang Zhu (Tianjin University), Junfeng Zhang (Tianjin University), Yan Yin (Tianjin University), Michael D Guiver (Tianjin University)\*

A strategy to make membranes with short-pathway through-plane orientated ion-conductive channels is described [1]. Previously, this has only been accomplished in a magnetic field by proton nonconductive metal oxide fillers. Here, under a strong magnetic field, a proton-conducting paramagnetic complex based on ferrocyanide-coordinated polymer and phosphotungstic acid is used to prepare composite membranes with highly conductive through-plane-aligned proton channels. This approach simultaneously overcomes the high water-solubility of phosphotungstic acid, preventing its leaching out of the membrane. The ferrocyanide groups in the coordination polymer continuously consume free radicals by a redox cycle, thus improving the long-term in situ membrane durability. The composite membranes exhibit outstanding proton conductivity, fuel cell performance and durability, compared with other types of hydrocarbon membranes and industry standard Nafion 212. [1] Nature Communications, in press. Publication date February 19th, 2019; DOI: 10.1038/s41467-019-08622-2

WEDNESDAY 4:30 pm - Ballroom 3

**32f - Novel sulfonated aromatic polymer membranes for breaking the proton selectivity-conductivity trade-off limitation in vanadium redox flow battery**

Tongshuai Wang (University of Illinois, Chicago), JunYoung Han (Rensselaer Polytechnic Institute), Kihyun Kim (Rensselaer Polytechnic Institute), Andreas Muenchinger (Max-Planck-Institute for Solid State Research), Klaus-Dieter Kreuer (Max-Planck-Institute for Solid State Research), Chulsung Bae (Rensselaer Polytechnic Institute), Sangil Kim (University of Illinois, Chicago)\*

Vanadium redox flow batteries (VRFBs) have received extensive attention due to its attractive features for the large-scale energy storage because of their design flexibility, absence of intercalation/deintercalation and stress build-up in electrodes, and safe operation. One of the most critical components in VRFB is an ion exchange membrane which can prevent cross mixing of the multivalence vanadium ions, while it still allows the transport of protons (or anions) to complete the circuit. However, the trade-off relationship of proton exchange membrane limits the energy efficiency (EE) of the VRFB due to low coulombic efficiency (CE) caused by vanadium ion cross over through the membrane or high membrane resistances. Anion exchange membrane suffers from poor chemical stability and low voltage efficiency due to low ion conductivity. In this study, we synthesized a series of novel sulfonated aromatic polymer membranes having high proton conductivity as well as selectivity which surpass the conventional proton conductivity-selectivity trade-off relationship. The effect of the pendent group structure on the membrane ion selectivity and battery performance was investigated. It was found that the incorporation of aromatic structures on the pendent groups effectively improved the proton conductivity and selectivity. The membrane with aromatic pendent groups (BPAr-F4) shows 3 times higher proton/vanadium ion selectivity than Nafion<sub>212</sub>. As a result, the VRFB cell equipped with the 80um-thick BPAr-F4 membrane shows significantly better performance in comparison to the cell with Nafion membranes, as high as 97.18% CE, 95.91% VE and 93.20% EE (vs. 75.14% CE, 96.12% VE and 72.22% EE of Nafion<sub>212</sub>; 91.30% CE, 95.63% VE and 87.62% EE of Nafion117) at 20 mA/cm<sup>2</sup>. Small-angle X-ray scattering studies indicates that their unique morphologies with narrow aqueous ionic domains which are well organized with acidic -SO<sub>3</sub>H groups results in the high proton selectivity and VRFB performance.