Thin Films
Room 317 - Session TF2-TuA

VSHOP Applications I, Membranes and Fluidics

Moderators: David S. Bergsman, University of Washington, **Siamak Nejati**, University of Nebraska-Lincoln

4:00pm **TF2-TuA-8 Selective Transport Through Organic Interfaces via Atomic and Molecular Layer Deposition: Durable Materials and Ion-Selective Membranes**, ***Tamar Segal-Peretz,*** Department of Chemical Engineering, Technion, Israel **INVITED**

The ability to control molecular transport through organic interfaces is crucial to a wide array of applications, including polymer and composite materials durability in harsh environmental conditions and membrane-based separations. In this talk, I will discuss how vapor-phase processing, specifically atomic layer deposition (ALD), vapor phase infiltration (VPI), andmolecular layer deposition (MLD) can be used to engineer organic interfaces with nanoscale precision for controlled molecular transport across them.

First, we utilized vapor-phase growth of inorganic materials on polymers and carbon fibers to enhance their durability under UV radiation and elevated temperatures. We showed that sequential VPI and ALD enable robust ZnO–polymer hybrid structures on poly(lactic acid) (PLA), where VPI creates subsurface and surface nucleation sites that promote conformal ZnO growth during ALD. While VPI or ALD alone provides limited protection, their combination yields polycrystalline ZnO coatings that reduce polymer photodegradation by more than two orders of magnitude, while preserving transparency in the visible range. In addition, we employed Al_2O_3 ALD on carbon fibers to reduce oxygen transport into the fibers and oxidative degradation at elevated temperatures. The Al_2O_3-coated fibers showed superior thermal durability and mechanical properties under these conditions.

Second, we used MLD to fabricate ion-selective polyamide membranes. MLD provides a unique route to synthesize ultrathin polyamide films with molecular-level control over thickness and chemistry. Using MLD, we grew ultrathin, ultrasmooth, and highly cross-linked aromatic polyamide selective layers directly on porous supports, achieving tunable, Angstrom-level controlled thickness in the 2-30 nm range. The MLD-based exhibited high water-ion and ion-ion selectivities. Beyond enhanced performance, MLD provides a powerful experimental platform for probing structure–composition–transport relationships with unprecedented precision. This approach opens new pathways toward rational design of polymer layers, building one molecular layer at a time.

4:30pm **TF2-TuA-10 Investigating the Impact of Membrane Hydrophilicity on Long- and Short-Chain PFAS Remediation via Molecular Layer Deposition**, ***Joelle Scott,*** *Jocelyne Booth, Kacey Taylor, Mathangi Venkatesh, Jay Werner, David S. Bergsman,* University of Washington

Per- and polyfluoroalkyl substances (PFAS) are a class of toxic contaminants in water that have become a topic of increasing concern. While long-chain PFAS have seen decreased use due to environmental regulation, short-chain PFAS continue to proliferate. Unfortunately, these smaller molecules are more environmentally mobile, harder to remove from water, and just as toxic, undermining environmental protection efforts. Membrane separations have been explored as a low cost technology to remove PFAS from water. However, membrane permeability usually must be sacrificed to be able to achieve high removal rates of these short-chain PFAS, like with desalination membranes. To combat this, using more hydrophilic membranes may increase the rejection of both long- and short-chain PFAS by reducing hydrophobic interactions between the membrane and PFAS compounds, resulting in an opportunity to improve rejection without compromising permeability. Current interfacial polymerization methods of membrane synthesis rely on identifying monomers that can be dissolved in immiscible solvents, greatly limiting the possible membrane chemistries that can be explored. Molecular layer deposition (MLD) is an alternative method for synthesizing thin film composite membranes that uses vapor-phase reactions, allowing for a wider range of selective layer chemistries to be explored. In this work, we use MLD to synthesize thin film composite membranes of different hydrophilicities, with the aim of investigating the impact of hydrophilicity on PFAS selectivity. To demonstrate the effectiveness of this technique for controlling membrane properties, polyurea and polyurethane films were deposited as membrane selective layers, and their film composition was confirmed using FTIR and XPS. These membranes were then examined for their pure water permeability and PFAS rejection, correlating these properties to their hydrophilicity to determine the impact of monomer chemistry. As part of this work, a polyurethane MLD process was developed and fully optimized for the first time. This work highlights the challenges of depositing thin films without interfacial polymerization, but the rewards of using techniques with independent compositional control for exploring polymer chemistry in membrane separations.

4:45pm **TF2-TuA-11 Vapor Phase Infiltration of Metal Oxides into Polymeric Water Treatment Membranes**, *Jiaman Wang, Chenhao Yao,* ***Bezawit Getachew,*** Rice University

Vapor phase infiltration (VPI) of metal oxides into polymeric membranes may offer a novel way to combine the benefits of polymeric and ceramic membranes and enable improved capabilities in water treatment membranes. In this paper, we investigate the infiltration of alumina into two types of membranes, namely polyamide nanofiltration (NF) membranes and commercial anion exchange membranes (AEMs). The infiltration is characterized by using X-ray photoelectron spectroscopy (XPS) to confirm the presence of metal oxide, quantify the amount of incorporation at the surface and as a function of depth, and probe the type of bonding taking place. Complementary SEM-EDX (Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy) and time of flight secondary ion mass spectrometry (ToF-SIMS) experiments show the distribution of the inorganic phase within the membranes. We find an increase in NaCl rejection from 90 to >95% for NF90 and MgSO4 rejection from 80 to 90% for NF270 membranes with minimal impact on water flux. For the AEMs, we find that the infiltrated membranes show improved resistance to degradation by chlorine without any changes in membrane resistance and permselectivity after infiltration. These results show that infiltration of metal oxides into polymeric membranes holds promise for improving the selectivity and stability of polymeric membranes without compromising other important performance metrics.

5:00pm **TF2-TuA-12 Molecular Layer Deposition of Salt Sieving Polyamide Membranes**, ***Brian Welch,*** University of Missouri*; Ruoke Cai, Tamar Segal-Peretz,* Technion Israel Institute of Technology, Israel **INVITED**

Membrane separations offer a vital pathway for recovering critical minerals such as lithium from magnesium-rich brines. However, conventional polymerization methods produce selective layers with poorly controlled molecular structure, resulting in low selectivity between Li^+ and Mg^{2+}. To overcome the limitations of solution-based polymerization, we used molecular layer deposition (MLD) to fabricate polyamide selective layers for nanofiltration (NF) and reverse osmosis (RO) membranes, using trimesoyl chloride/piperazine (NF) and trimesoyl chloride/m-phenylenediamine (RO) precursors. MLD-grown polyamide films exhibited structural advantages, including high crosslinking, high mass density, low surface roughness, morphological homogeneity, and precise thickness control. Inverse gas chromatography measurement of surface energy revealed that amine-terminated cycles were free of surface defects. MLD NF membranes deposited at 1.3 Å/cy achieved Li^+/Mg^{2+} selectivity as high as 35, compared to 3 for commercial membranes, while maintaining comparable Li^+ flux. While the Li^+/Mg^{2+} selectivity of conventional NF membranes relied on Donnan exclusion arising from strong surface charges, MLD NF membranes achieved high selectivity with negligible surface charge through molecular sieving via 5 ± 1 Å ultramicropores. While conventional, solvent-based synthesis results in selective RO layers with overall thickness > 100 nm, MLD RO films grew at a rate of 2.4 Å/cy, enabling fabrication of functioning membrane films as thin as 2 nm. By probing the extreme low end of thickness, we improved water flux, but ultimately reached a performance limit, demonstrating that selective films with thickness below their Bjerrum length exhibited reduced salt selectivity due to decreased dielectric self-energy. These results establish a high-precision platform for probing and optimizing molecular transport in thin-film composite membranes and advancing membrane materials.

5:30pm **TF2-TuA-14 Tertiary and Aromatic Polyurea Films Deposited Using Molecular Layer Deposition as a Method of Producing Cationic Thin Film Coatings for Use in Microfluidic Design**, ***Jay Werner***[1], *David S. Bergsman,* University of Washington

The application of cationic thin film coatings has gained interest as a method of producing antibacterial surfaces which can passively resist bacterial contamination and reduce the spread of infectious microbes. One common method of producing these cationic surfaces is through the

[1] **JVST Highlighted Talk**

exposure of surface amine groups to methyl iodide to produce quaternary ammonium compounds (QACs). These films are typically deposited from the liquid phase using spin coating, spray coating, or dip coating, but these coating methods can be difficult or impossible to implement effectively for high aspect ratio or enclosed microfluidic devices. Molecular layer deposition (MLD) is a vapor phase process involving the exposure of a surface to reactive precursors in a cyclic manner, forming a polymer film layer by layer in a highly precise and conformal way. To vaporize precursors, they must be neutrally charged, but the deposition of a polyurea film with tertiary or aromatic amine sites could be used as a substrate for post-synthetic surface quaternization with liquid or vapor-phase treatment with methyl iodide.

In this work, we investigate the formation of polyurea MLD chemistries based on low melting point 2,4-toluene diisocyanate (TDIC) combined with substituted diamines including bis(2-aminopropyl)(methyl)amine (BAPMA) and 2,6-diaminopyridine (DAP). These precursors enable incorporation of tertiary and aromatic nitrogen functionalities into polyurea thin films, providing reactive sites for subsequent in situ or ex situ quaternization. The resulting substituted polyurea films are investigated as candidate substrates for vapor-phase fabrication of cationic antimicrobial coatings compatible with microfluidic device architectures, characterizing their film thickness, composition, and surface charge before and after exposure to methyl iodide. These results demonstrate a new avenue towards the creation of films with MLD and a possible new approach toward the functionalization of surfaces with cationic coatings.

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