Nanoscale Science and Technology
Room 114 - Session NS1-MoM

Water and Ionic Transport at the Nanoscale
Moderator: Mark Hersam, Northwestern University

8:45am **NS1-MoM-3 Phase Separation and Oxygen Diffusion in Resistive Memory*, Yiyang Li,*** University of Michigan **INVITED**

Resistive memory is a promising technology that conducts memory and computation through the migration of oxygen in transition metal oxide. Understanding the mechanisms of oxygen migraiton is critical towards understanding the functionality of resistive memory devices. In this talk, we present our recent research on the materials thermodynamics and kinetics principles that govern ion motion in oxide-based resistive memory. Using a combination of device measurements, materials characterization, and multiscale physical modeling, we find that oxygen vacancies do not obey Fick's First Law of diffusion as conventionally believed, but instead undergo composition phase separation, which enables diffusion against the concentration gradient. This work yields design rules for nonvolatile memory devices based on composition phase separation.

9:15am **NS1-MoM-5 Advanced Aqueous Separations Using Membranes with Tailored 1D and 2D Confinement*, Seth Darling,*** Argonne National Laboratory

Solute transport in confined environments is a subject of profound interest and ongoing exploration, with recent advancements pointing toward transformative possibilities. Traditional hindered transport theory, a longstanding framework for understanding solute movement through cylindrical pores, underscores the significance of convective and diffusive hindrance in impeding solute permeation, thereby limiting sharp solute separations by membranes. However, breakthroughs in membrane technology, particularly the utilization of near-perfect isoporous membranes, offer new avenues to surmount these limitations. By leveraging nanofabricated, defect-free silicon nitride membranes and employing recirculated feed strategies to enhance solute-membrane interactions, we have achieved encouraging solute rejections, effectively barring solutes larger than the pore size while facilitating the passage of smaller solutes. This advancement not only represents a departure from historical constraints but also holds promise for unprecedented membrane separations through meticulous process design and tight pore-size distributions. Concurrently, the integration of two-dimensional (2D) materials into membranes introduces a distinct paradigm for ion transport and separation applications. These membranes exploit interlayer galleries to drive separation and selectivity, with specific transport properties shaped by chemical and structural modifications within the interlayers. A novel approach involving exfoliated and restacked phyllosilicate minerals with molecular crosslinkers allows precise control over interlayer spacing, influencing ion diffusivities in the resulting crosslinked 2D membranes. These membranes, characterized by tunable ion diffusivities, provide a platform for systematic studies of confined ionic transport, offering insights into fundamental mechanisms governing solute movement in nanoconfinement and paving the way for synergistic advancements in membrane-based separation technologies.

9:30am **NS1-MoM-6 Radioactive Tracer Diffusion through TPT-CNMs*, Andre Beyer,*** *N. Khayya, A. Gölzhäuser,* Bielefeld University, Germany

In recent years, Carbon Nanomembranes (CNMs) have emerged as an innovative class of 2D materials known for their exceptional combination of high selectivity and permeation properties, with a particular emphasis on p-[1,1',4',1"]-terphenyl-4-thiol (TPT)-CNM with a thickness of about 1 nm. Such CNMs combine a rapid water permeation with ultrahigh ionic exclusion in aqueous solution [1]. Here, we report permeation measurements of carbon dioxide and water through TPT-CNMs, which were conducted with concentration-gradient-driven transport of radioactive tracer molecules, specifically [3H] H_2O, [14C] $NaHCO_3$, and [32P] H_3PO_4. Our investigation explores the impact of the pH value on the diffusion process. The equilibrium ratio of carbon dioxide and the corresponding anions change with the pH value. Therewith, an independent characterisation of the diffusion of carbon dioxide and its anionic forms appears to be feasible. Considering concentration polarization and outgassing effects, our results align with previously obtained radioactive diffusion data for a neutral pH value of 7 [2]. Interestingly, despite the electrostatic barrier associated with TPT-CNM in neutral aqueous environments, our observations indicate enhanced permeation of anions in the basic range of pH.

[1] Y. Yang et al., ACS Nano 12, 4695 (2018); Y. Yang et al., Adv. Mater. 32, 1907850 (2020).

[2] R. Dalpke, A. Dreyer, R. Korzetz, K. J. Dietz, and A. Beyer, J. Phys. Chem. Lett. 11, 6737 (2020).

9:45am **NS1-MoM-7 Molecular-Resolution Elucidation of Ice Defects Formed by Liquid Water Crystallization*, Jingshan Du,*** Pacific Northwest National Laboratory*; S. Banik,* University of Illinois - Chicago*; H. Chan,* Argonne National Laboratory*; B. Fritsch,* Helmholtz Institute Erlangen-Nürnberg for Renewable Energy, Germany*; Y. Xia,* University of Washington*; A. Hutzler,* Helmholtz Institute Erlangen-Nürnberg for Renewable Energy, Germany*; S. Sankaranarayanan,* University of Illinois - Chicago*; J. De Yoreo,* Pacific Northwest National Laboratory

Despite the ubiquity of ice, defects in ice formed by water crystallization have never been directly observed on the molecular scale. Here, we report the stabilization and Ångstrom-resolution electron imaging of ice I_h crystallized from liquid water. Combining lattice mapping and molecular dynamics simulations, we show that ice is highly tolerant to nanoscale defects such as misoriented subdomains and trapped gas bubbles, which are stabilized by molecular-scale structural motifs. We discovered subdomain-rich regions near the defective crystal edges despite the structure appearing single-crystalline according to diffraction criteria. These subdomains connect via low-angle grain boundaries with flat energy landscapes as a function of tilt angles, showing the high tolerance of ice to defect structures. Furthermore, bubble surfaces adopt low-energy nanofacets and create negligible strain fields in the surrounding crystal. These bubbles can dynamically nucleate, grow, migrate, dissolve, and coalesce under electron irradiation and be monitored in situ near a steady state. This work opens the door to understanding water crystallization behaviors at an unprecedented spatial resolution and provides new research paradigms to the theory, modeling, and forecasting of ice crystallization and melting in environmental, biological, and material systems.

10:00am **NS1-MoM-8 Reduce Liquid Waste and Improve Throughput in CVD and ALD Processing*, Kathleen Erickson,*** MSP - A Division of TSI

Liquid Flow Controllers (LFCs) are routinely used with vaporizers in gas-phase processing to improve process repeatability, precision and adjustability. In the microelectronic industry LFCs are used to vaporize liquid precursors for Chemical Vapor Deposition (CVD) or Atomic Layer Deposition (ALD). Due to high precision requirements and long LFC flow control response/stabilization times (time to reach and maintain ±1% of set-point), liquid or vapor divert schemes are often used in CVD and ALD. In this scenario, the liquid or vapor is diverted to exhaust until the LFC is able to reach and stably maintain the setpoint. Legacy LFCs can have response times on the order of 4-9 seconds. These long stabilization times, result in significant time sending vapor/liquid to the diverter line – meaning more liquid waste. More liquid is consumed, pumps are exposed to more liquid, and remediation systems have a higher load. Increased liquid waste negatively impacts cost of ownership in increased liquid precursor source cost, reduced pump lifetime, and increased maintenance requirements.Additionally, it worsens the environmental impact of these semiconductor processes. As more and more semi processes run short processing times, this long response time is becoming increasing problematic to throughput as well. For long processes, LFC response times have a relatively small impact on throughput; in a 150 second process, a 3 second liquid flow stabilization time only adds 2% to the processing time - still significant, but perhaps not intolerable. However, for short process times, like short pulse CVD or ALD, the stabilization time of the LFC can become a much larger percentage of the processing time.For example, in a 6 second short pulse CVD process, a 3 second response time increases deposition times by 50%.

This presentation will introduce a new Liquid Flow Controller (Turbo LFC) designed specifically for semiconductor processing. The Turbo LFC can reach ±1% of set-point within 0.3s – a significant improvement over conventional LFCs. The fast response time is a result of a high-speed sensor, which can also provide advantages in process control. A fast sensor enables a faster feedback control loop which can result in tighter control. This high-speed LFC also opens the possibility for measuring the delivered mass of vapor pulses (0.05 – 1+s), providing an alternative to ALD valves, which provide no feedback on mass flow rates and are affected by line pressure and temperature. Details on Turbo LFC design and performance data will be reviewed, including the accuracy, repeatability and response time, and the impact of ambient temperature and line pressure on performance.

Author Index

Bold page numbers indicate presenter

— B —
Banik, Suvo: NS1-MoM-7, 1
Beyer, Andre: NS1-MoM-6, **1**
— C —
Chan, Henry: NS1-MoM-7, 1
— D —
Darling, Seth: NS1-MoM-5, **1**
De Yoreo, James: NS1-MoM-7, 1
Du, Jingshan: NS1-MoM-7, **1**
— E —
Erickson, Kathleen: NS1-MoM-8, **1**
— F —
Fritsch, Birk: NS1-MoM-7, 1
— G —
Gölzhäuser, Armin: NS1-MoM-6, 1
— H —
Hutzler, Andreas: NS1-MoM-7, 1
— K —
Khayya, Neita: NS1-MoM-6, 1
— L —
Li, Yiyang: NS1-MoM-3, **1**
— S —
Sankaranarayanan, Subramanian: NS1-MoM-7, 1
— X —
Xia, Ying: NS1-MoM-7, 1