Impact of Surface-Induced Ordering on Measurements of Bulk Ionic Conductivity in Block Copolymer Electrolytes

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Lamellar block copolymers based on polymeric ionic liquids (PILs) show promise as electrolytes in electrochemical devices. Accurate measurements of the bulk ionic conductivity are necessary to inform structure-property relations. However, when measuring ionic conductivity through electrochemical impedance spectroscopy (EIS) or broadband dielectric spectroscopy (BDS), the extracted value may be more than 10x higher when measured with an in-plane rather than through-film geometry. We propose that this anisotropy stems from differences in the surface and bulk structures. Specifically, preferential interactions between one block and a surface (either electrode or air) will produce wetting layers and drive short-range stacking of lamellar domains. This phenomenon will produce continuous PIL layers across the surface of the block copolymer film, whereas the bulk structure is comprised of randomly oriented grains. The formation of wetting layers and surface-induced lamellar stacks is easily confirmed through contact angle measurements and island/hole studies of ultrathin films, respectively. By systematically varying the surface structure, we show that through-film measurements of the ionic conductivity are insensitive to wetting layers and lamellar stacking. This leads us to conclude that in-plane measurements yield inflated values due to continuous PIL domains across the surface, which offers a low-resistance pathway for ion transport, while through-film measurements probe the true bulk ionic conductivity. Notably, as many prior studies of these materials employed in-plane measurement techniques, we find that the bulk ionic conductivity in these materials is much lower than previously thought. Ongoing work suggests that the depressed ionic conductivity is a consequence of poor connectivity among PIL domains, which could be corrected by manipulating the block copolymer composition and/or processing conditions.

Biography: **Gila Stein** received her BS in Chemical Engineering from Drexel University in 2002, and obtained a PhD in Chemical Engineering from the University of California, Santa Barbara, in 2006. She then joined the National Institute of Standards and Technology, where she was a National Research Council Postdoctoral Fellow in the Center for Nanoscale Science and Technology from 2007-2008. Stein moved to the University of Houston as an Assistant Professor of Chemical and Biomolecular Engineering in 2009, received the Henley Professorship in 2012, and was promoted to Associate Professor in 2015. She joined the University of Tennessee as the Prados Associate Professor of Chemical and Biomolecular Engineering in 2016 and was promoted to Professor in 2020.

The Conformations of Polyzwitterion Chains and Its Coacervates in Aqueous Solutions Studied by ORNL Small-Angle X-ray Scattering Instrument

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Polyzwitterions are considered as model synthetic analogues of intrinsically disordered proteins. Based on this analogy, polyzwitterion chains in dilute aqueous solutions are expected to attain either globular or random coil conformations. Addition of salt is expected to open up these conformations either due to screening of dipole-dipole interactions or as a result of ion-binding to zwitterion groups. To verify these hypotheses about conformations of polyzwitterion chains, we study dilute aqueous solutions of a poly(sulfobetaine methacrylate) (PSBMA) using small angle X-ray scattering (SAXS) and dynamic light scattering (DLS). It is found that added salt leads to non-monotonic changes in the radius of gyration and hydrodynamic radius exhibiting an increase at low salt concentration followed by a decrease at higher salt concentration, which are called anti-polyelectrolyte and polyelectrolyte effects, respectively. Implications of these findings on studying coacervates based on polyzwitterions will be presented. For understanding the effects of zwitterions, conformation of PSBMAs were compared with those of the polymers of the same backbone but containing no explicit charges on side groups such as poly(2-dimethylaminoethyl methacrylate)s (PDMAEMA). We will also introduce a versatile ORNL SAXS instrument that is open to public through CNMS user program.

Biography: Jong Keum is a Neutron Scattering Scientist at the Neutron Scattering Division (NSD) and Center for Nanophase Materials Sciences (CNMS), Oak Ridge National Laboratory (ORNL). He received a Ph. D. degree in Chemistry from the State University of New York (SUNY) at Stony Brook in 2007. After a couple of post-doctoral appointments at the Case Western Reserve University (CWRU) and Oak Ridge National Laboratory (ORNL), he joined NSD/CNMS as a staff member in 2013. Jong's major research has focused on the nano- and mesoscale structure and physics of soft matters and nanomaterials, where he primarily utilizes X-ray and neutron small-angle X-ray scattering, reflectivity and diffraction.

Coarse-Grained Modeling of Ion Transport in Solid Polymer Electrolytes

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Solid polymer electrolytes are of interest as safer, nonflammable battery electrolytes. Microphase separating copolymers in particular are attractive because one microphase can solvate and allow transport of ions, while another provides additional mechanical strength. However, the relatively low ion conductivity through such materials remains a challenge; strategies to improve cation conduction include using larger anions or a higher dielectric strength polymer (which more strongly solvates ions). These strategies effectively decrease the strength of ion-ion interactions and thus can reduce ion agglomeration and correlated cation/anion motion. However, strong ion-polymer interactions also slow ion motion, and when the polymer more strongly solvates smaller cations versus larger anions, this can lower the transference number (fraction of the conductivity contributed by the cation). We study these competing effects using coarse-grained molecular dynamics (MD) simulations which include a $1/r^4$ potential to capture size-dependent ion-monomer and ion-ion solvation effects. This is the same form as the interaction between an ion and an induced dipole and allows us to capture the experimentally observed trends in lamellar domain spacing and ion conductivity versus ion concentration. The impacts of ion size and polymer dielectric strength, as well as the impact of tethering anions to the polymer chain, on ion correlations, diffusion, and cation conductivity in salt-doped homopolymer and block copolymer systems will be discussed.

Biography: Lisa Hall is a Professor at the Ohio State University. She joined OSU in 2012, having completed her Ph.D. with Kenneth Schweizer at the University of Illinois and a subsequent postdoctoral appointment with Amalie Frischknecht and Mark Stevens at Sandia National Laboratories. Her research group uses statistical mechanical theory and molecular dynamics simulations to study molecular behavior and properties of nanostructured polymeric materials. In 2021 she received the Owens Corning Early Career Award from the Materials Engineering & Sciences Division of the American Institute of Chemical Engineers.

AI/ML Strategies in Charged Polymer Materials: Continuous Flow Polymer Synthesis and Reactions

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The use of artificial intelligence and machine learning (AI/ML) in polymer materials have appended the ability to rapidly optimize synthetic routes and manufacturing. The use of Bayesian and statistical methods enable the application of logic derived design and regression analysis into an otherwise trial-and-error approach in polymer synthesis, fabrication, and characterization. We demonstrate in this talk the use of continuous flow reaction chemistry to enable unit operation optimization and the possibility of autonomous design and synthesis with a hierarchical approach and learning. We are interested in the synthesis of charged polymer systems including reactions in aqueous media. There is a high possibility that a combination of P,V,T and flow rate control enables new methods of copolymerization and the ability to use kinetics as a handle for optimized macromolecular properties and design for controlled yield. For charged polymers, it will go beyond just MW control but possible with charge distribution, charge density, copolymers, and block copolymers. Deuteration is also important. The automation for online monitoring is a future possibility with improved instrumentation and development of a feed-back loop learning for possible deep learning (DL) development.

Biography: Rigoberto Advincula is a Governor's Chair Professor at the Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, TN, USA. He is also a Group Leader at Oak Ridge National Laboratory (ORNL), Center for Nanophase Materials Sciences (CNMS). He is a Fellow of the American Chemical Society (ACS), Fellow of the Polymer Science and Engineering Division (ACS), Fellow of the Polymer Chemistry Division (ACS), and a Fellow of the Royal Society of Chemistry. He received the distinguished Herman Mark Scholar Award in 2013. In 2018, he was elected National Academy of Science and Technology (NAST), Philippines. In 2022 he received the Lifetime Distinguished Accomplishment Award from the University of the Philippines (UPAA). He has been appointed to the World Economic Forum, Advanced Materials Council. He is Editor-in-Chief of MRS Communications and was formerly Editor of Reactive and Functional Polymers. He has held several visiting Professor positions including Waseda University in Japan and the Max Planck Institute for Polymers Research in Germany. His group does research in polymer materials, nanocomposites, colloidal science, 3D printing, hybrid materials, and ultrathin films for applications from smart coatings to biomedical devices. He is passionate in mentoring students and helping other countries in their STEM programs.

Machine Learning Based Pipeline for Analysis of Neutron Reflectivity Data from Thin Films of Charged Polymers

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Thin films of ionic polymers are of great technological interest due to their relevance to solid polymer electrolytes and energy storage. There is active research on controlling morphology in these films to modify ion transport, a process affected by adsorption of ionic groups on conductive surfaces. However, visualizing these adsorbed layers (~5-10 nm) is challenging and requires characterization tools capable of capturing both vertical and lateral structures, such as grazing incidence neutron scattering, providing vertical (specular reflection) and lateral structures (off-specular scattering) of ionic polymers. While specular neutron reflectivity extraction is routine, analyzing off-specular scattering remains complex. Here, we have worked towards a machine learning (ML) workflow using simulated and experimental data. It relates thin film structure with ionic polymers to their specular spectra. Our workflow improves understanding of ionic polymer electromechanical responses, speeding up desired structure discovery.

Biography: Dustin Eby is a former SULI intern at the Center for Nanophase Materials Sciences (CNMS), Oak Ridge National Laboratory (ORNL). He has a B.Sc. in mathematics and computer science from the University of Denver, with a focus on optimization, stochastic methods, machine learning, and algorithm analysis. His research while at ORNL focused on developing machine learning frameworks and models for the analysis of neutron reflectometry data.

Soft Matter Microscopy in the Age of AI for Charged Polymers and Hybrid Complexes

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Tailored polymer architectures and controlled assembly represent a key approach to guide the formation of functional nanostructures for optimized charge transport and energy storage. (1-2) To understand the underlying intermolecular interactions and fascinating structures, we combine AI and low-dose analytical TEM, in efforts towards automated segmentation, labeling, and tracking. Low-dose electron diffraction provides in-plane information, which is complementary to experiments such as neutron reflectivity and grazing-incidence X-ray. Energy filtered TEM provides low-dose nanoscale chemical mapping with minimum morphological impact. As an example for charge transport optimization, a centipede polymer / small molecular blend is examined in nanostructural details herein, while a charged polymer-guided salt complex is used as an example for improved solid electrolyte. A beginner-friendly discussion will be provided for both AI and soft matter microscopy as part of the tutorial, which includes TEM sample preparation, imaging procedures, common AI algorithms, and model deployment.

1. J Chen, Nanomaterials 11 (9), 2405, 8, 2021
2. J Chen, etal, SmartMat 2 (3), 367-377

Biography: Dr. Jihua Chen has been a R&D staff member at the Center for Nanophase Materials Sciences (CNMS), Oak Ridge National Laboratory (ORNL) since 2011. He obtained a PhD in Macromolecular Science and Engineering from the University of Michigan-Ann Arbor in 2006. Working at the conjunction of soft electronics, battery, medicine, and data science, he is applying AI, soft matter, and microscopy to tackle problems in manufacturing and healthcare. He served or is serving as a committee member of the Governmental Affairs Subcommittee, New Meetings Subcommittee, Impact of Materials on Society subcommittee at the Materials Research Society, as well as on the executive committee of APS Data Science Group. He organized symposiums for Microscopy & Microanalysis meetings, American Chemical Society, American Physical Society, and ORNL Soft Matter Symposium. Dr. Chen also serves as a proposal reviewer for a number of funding agencies in Europe and US, as well as a manuscript reviewer for 30+ journals (over 400 times) including Advanced Materials, Chemical Society Review, Energy and Environmental Sciences, ACS Applied Materials & Interface, and IEEE Electron Device Letter. Dr.Chen authored and co authored 160+ scientific publications, over 40 talks, with a H-index of 55 and over 10k citations on Google Scholar.

Ion Transport and Segmental Dynamics in Polymer Electrolytes and Composite Cathode

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Polymer electrolytes are promising to enable the next generation batteries with higher energy density and improved safety. The intrinsic and extrinsic interfaces that a polymer electrolyte faces in a practical battery may profoundly impact its transport properties. In this presentation, I first discuss the structure-property relationship of fluorinated polyether copolymers consisting of crosslinked network of poly(ethylene oxide) segments and perfluoropolyether segments. The effect of the phase separated morphology on the thermal and electrochemical properties will be elucidated. In a second case, I examine the effect of interfaces on ion transport in a polymer based composite cathode consisting of $LiFePO_4$ (LFP), carbon and PEO with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). The structure and dynamics of PEO and lithium ion mobility are studied by small angle neutron scattering and quasi-elastic neutron scattering. The results show that Li ion mobility in PEO/LiTFSI in the composite cathode is only 30% of the bulk electrolyte. This suggests a key bottleneck that limits the rate performance of polymer-based solid-state batteries originates from the sluggish ion transport in the polymer electrolyte confined in the cathode.

Biography: Chelsea Chen is a polymer physicist by training. She got her PhD in Macromolecular Science and Engineering from the University of Michigan, Ann Arbor. Her dissertation topic is the control of the spatial distribution of nanoparticles within a thin film polymer host. After completion of PhD, she did a postdoc at UC Berkeley/Lawrence Berkeley National Lab, studying proton-conducting block copolymer membranes using cryo-transmission electron microscopy and small angle X-ray scattering. Before joining ORNL, She worked as a senior chemist at Dow Chemical. Her research at ORNL focuses on understanding the ion transport in polymer/ceramic composite electrolytes, electrolyte/electrode interfaces and the development of solid-state batteries.

Low-frequency dynamics in ionic materials: going beyond dc conductivity

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Direct current (dc) conductivity is one of the most important and prominent properties that can be extracted from broadband dielectric spectroscopy measurements of ionic materials. In this talk, we discuss our recent effort to go beyond such a simple analysis and gain insights into the conduction mechanisms of ionic liquids by examining the fine features of their dielectric spectra. We show that the derivative of real permittivity of ionic liquids progressively broadens at low frequencies when the glass transition is approached from above. Numerical simulations with the random barrier model reveal that the observed low-frequency broadening is associated with the contributions from high activation energy pathways, suggesting a direct connection between relaxation time distribution and barrier distribution. While the overall prediction of the random barrier model about ac conduction is insensitive to the distribution of activation energy in the extreme disorder limit, the fine features of the derivative spectra contain further information about the energy landscape. These results demonstrate the usefulness of derivative analysis of the dielectric spectra of ionic liquids and glasses at low frequencies, where materials exhibit individual characteristics despite apparent ac universality.

Biography: Yangyang Wang is a staff scientist at the Center for Nanophase Materials Sciences (CNMS), Oak Ridge National Laboratory. His research focuses on understanding the dynamics and rheology of soft materials through the combination of experimental techniques (rheology, scattering, and dielectric spectroscopy) and molecular simulations. He earned his PhD in Polymer Science from the University of Akron in 2010. Before joining CNMS in 2014, he worked as a postdoctoral researcher in the Chemical Sciences Division of the Oak Ridge National Laboratory.
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