Abstract: Ion-conductive polymers (ionomers) have been widely used as the solid-electrolyte in energy conversion devices, such as polymer-electrolyte fuel cells (PEFCs), redox flow batteries and electrolyzers, to facilitate selective transport of ionic and gaseous species. Ionomers such as perfluorosulfonic-acid (PFSA) primarily function as the separator-electrolyte in these devices due their high ion conductivity and chemical-mechanical stability. Yet, for the desired new clean-energy paradigm, ionomers with improved stability and modified functionalities are needed. In PEFCs, for example, ionomers exist as nanometer-thick electrolyte “thin film” to facilitate transport of ionic and gaseous species to the catalytic particles. Once confined to these thicknesses (< 100 nm), ionomer properties change drastically from the bulk (membrane) and are significantly more influenced by interfacial and ionic interactions. Thus, throughout this thickness range, ionomer morphology and behavior are controlled by the interactions related to chemical and mechanical properties, which impact the interplay between transport and stability. It is this interplay that ultimately affects the performance and durability of these materials in electrochemical devices. This talk explores structure-property relationships of PFSA-based ionomers of various thicknesses - from micrometer to 10’s of nanometers - to examine how their performance and functionality are governed by chemical-mechanical interactions in different environment. The underlying origins of these interactions are elucidated by correlating mechanical and transport properties of an ionomer with its morphology, which is characterized in-situ, using transmission and Grazing-Incidence synchrotron x-ray scattering techniques. I will show how material interactions influence deviations in ionomer structure-functionality due to confinement and chemistry so as to develop a holistic view of ionomers across lengthscales and discuss its implications for device performance and durability.