Fast and Cooperative Ion Transport in Polymer Based Materials (FaCT)
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Mission Statement*: To understand and control fast, correlated ion and proton transport at multiple length and time scales in polymer-based electrolytes to overcome the current limitations of energy storage and conversion technologies.*

A major bottleneck limiting the advancement of energy storage and conversion technologies is the development of multifunctional, selective, and highly conductive membranes and solid electrolytes. Polymer-based electrolytes are amongst the most promising materials for next-generation applications due to their high electrochemical stability, mechanical flexibility, processibility, and their ability to maintain electrical contact over large temperature variations (good adhesion properties) better than their more brittle ceramic counterparts. Furthermore, they provide an ideal platform to support next generation energy storage architectures, such as those relying on the interdigitation of an electrolyte with the electrode. A grand challenge lies in the fact that polymer membranes, however, have yet to achieve the necessary conductivity and selectivity for fast ion transport and suffer from water management issues that restrict operating temperatures due to the need for water (i.e., hydrogen bonding networks) to transport protons. Efforts to improve conductivity, mechanical modulus, flexibility, and safety, by combining polymers and superionic ceramics, have thus far failed to provide the necessary conductivity.

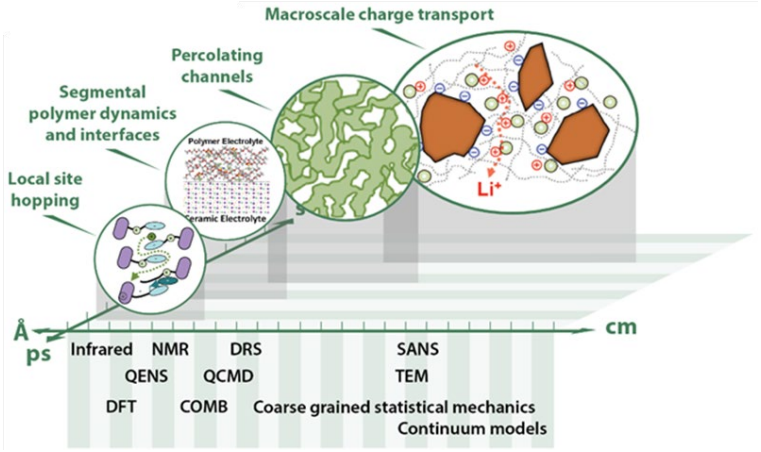

Figure 1 Length and time scales of experiments and theory relevant to the FaCT mission. (QENS = quasielasitc neutron scattering, BDS = broadband dielectric NMR = nuclear magnetic resonance, DFT = density functional theory, DRS = diffuse reflectance spectroscopy, QCMD = quartz crystal microbalance with dissipation monitoring, COMB = charge-optimized many-body potential, SANS = small-angle neutron scattering, and TEM = transmission electron microscopy.)

This center seeks to build a predictive, data-driven, physics-based mechanistic model of ion and proton transport in polymers and polymer-ceramic composites to enable the targeted design of next-generation energy storage and conversion materials. *Materials-specific experimental and computational data covering a broad range of length and time scales will inform macroscale descriptions of charge transport to accelerate the design of polymer electrolytes with fast, correlated ion transport.* A foundational goal is to understand the nanoscale origins of ion and proton conductivity by identifying the mechanisms that determine how ions and protons move in polymers and composites on a microscopic (0.1–10 nm) scale and to correlate these movements to macroscale transport properties. In essence, we seek to discover new systems with superior charge transport to what is available today. Emphasis will be placed on determining (i) how ion diffusion/hopping can be decoupled from polymer segmental dynamics and how to significantly reduce the energy barriers for charge (alkali ions and protons) hopping in polymers; (ii) how conductivity is enhanced by specific ion channel morphologies and polymer solvation microenvironments; (iii) how ions move along or across dissimilar interfaces; and (iv) how specific chemical additives can accelerate charge transport and how they can be introduced in microstructured channels and at interfaces to improve conductivity. This will enable us to (i) increase ion mobility, (ii) improve ion solvation

and dissociation, (iii) devise new chemical systems for fast hopping transport, and (iv) promote fast, correlated charge transport in a material across nanometer to millimeter length scales. This research will concentrate on (i) small classical cations (Li^+ and Na^+) diffusing through a matrix, and (ii) protons where hopping transport and dynamic hydrogen bonding can be leveraged. As model polymer systems, we will initially focus on single ion conducting polymers and polymer-composites relevant to future clean-energy technologies. Single ion conductors provide selective ion transport and have significant advantage for many applications, in comparison with dual ion conductors. These systems are chosen to allow for one-to-one, seamless, comparisons, across multiple length and time scales, between theory and experimental synthesis and characterization efforts. To achieve our goal, *FaCT* is built upon two thrusts and a crosscut:

Thrust 1: Unveil the mechanisms driving correlated alkali ion and proton transport in polymers. The goal of this Thrust is to understand and realize new mechanisms of superionic conductivity (Li^+, Na^+, H^+) in polymer-based materials (i.e., > 1 mS/cm at room temperature). ***Key questions:*** What are the fundamental physics controlling charge transport in polymers and what are the microscopic mechanisms that determine energy barriers for ion hopping? Why does correlated ion motion suppress charge transport in polymeric materials, while it enhances charge transport in superionic glasses?

Thrust 2: Elucidate the mechanisms controlling correlated ion transport at the polymer–ceramic interface and reducing interfacial ion transport barriers. This Thrust seeks to elucidate the microscopic mechanisms controlling ion transport along and across polymer–ceramic interfaces, to design modified interfaces with reduced ion diffusion barriers. ***Key questions:*** How do interfacial chemistries and structures alter ion transport and dissociation? How do changes in interfacial polymer dynamics correlate with ion transport? What is the origin of the interfacial charge–transfer barrier and how can it be minimized?

Crosscut: Design through computation, theory, and materials informatics. The crosscut goal is to leverage fundamental knowledge obtained from the Thrusts to enable the design of fast ion conducting polymer and polymer-ceramic electrolytes. ***Key questions***: How can representation learning be utilized to combine experimental and simulation data to discover high-performing polymer electrolytes with superior charge transport? How can theoretical and computational approaches with vastly different data types be combined in an interconnected, seamless, multiscale manner to predict bulk and interfacial properties critical for fast, cooperative ion-conducting polymer-based electrolytes?

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