CPP 13: Charged Soft Matter, Polyelectrolytes and Ionic Liquid

Time: Tuesday 9:30–11:15 Location: H38

Invited Talk CPP 13.1 Tue 9:30 H38

Insights into degradation mechanisms in Li-based batteries and advantages of polymer coatings — •Neelima Paul — Heinz Maier-Leibnitz Zentrum (MLZ), TU München, Lichtenbergstr. 1, 85748 Garching, Germany

Lithium-ion batteries are present in portable electronics, electric vehicles and grid-scale energy storage and are an inherent part of our daily life. They offer high energy density, high power density, stable temperature performance, and are safe. However, they eventually suffer from capacity fade due to some intrinsic degradation mechanisms, and thus have a limited cycle life. To increase their lifetime, knowledge of the responsible degradation/aging mechanism is crucial and most beneficial if determined without destructive disassembly of the battery. I will demonstrate how parameters responsible for aging such loss of mobile Li inventory, active material degradation, metallic Li plating, can be monitored and quantified using both operando and post-mortem neutron techniques. Thereafter, I will describe the main degradation mechanism in Li-metal batteries and show how this can be overcome by applying viscoelastic polymer coatings with a specific mechanical strength to the anode surface.

CPP 13.2 Tue 10:00 H38

Electrostatically Cross-Linked Reversible Gels - Effects of pH and Ionic Strength — Roman Staňo[1,4], •Peter Košovan[1], Andrea Tagliabue[2], and Christian Holm[3] — [1]Faculty of Science, Charles University, Prague, Czechia — [2]Universitá degli Studi dell Insubria, Como, Italy — [3]Institute for Computational Physics, University of Stuttgart, Germany — [4]University of Vienna, Austria

Mixing of oppositely charged macromolecules can lead to the formation of electrostatically cross-linked coacervate gels. In this simulation study, we determine the conditions under which four-armed star copolymers with charged end-blocks are able to form such coacervate gels. The cationic charged blocks consist of quenched charges, whereas the anionic blocks contain pH-responsive weak acid groups. We used the Grand-reaction method to determine the phase stability, equilibrium composition, and structural properties of these systems in equilibrium with a supernatant solution at various pH levels and salt concentrations. Depending on the pH and hence on the charge state of the polyanion blocks, we observed the emergence of three regimes: a solution, a sol of isolated star clusters, and a gel*percolating network of stars. Moreover, we demonstrate that the charge state of the stars in the gel phase can be well described by the ideal Henderson-Hasselbalch (HH) equation, despite the presence of strong interactions violating ideality. We can explain this surprising result by cancellation of two stongly non-ideal effects. This observation explains why various experiments on coacervate gels can be well described by the HH equation, although its assumption of ideality is violated.

CPP 13.3 Tue 10:15 H38

Temperature Dependence of PSS diffusion in multilayers of entangled PDADMA: more than one diffusion constant — •Annekatrin Sill[1], Peter Nestler[2], Peter Thran[1], and Christiane A. Helm[1] — [1]University of Greifswald, Institute of Physics, D-17489 Greifswald, Germany — [2]ZIK HIKE-Biomechanics, University of Greifswald, D-17489 Greifswald, Germany

Layer-by-layer assembly is a widely used tool for engineering materials and coatings, but the dynamics of the constituent polymer chains remain poorly understood. Using neutron reflectivity, the vertical diffusion of polyanion PSS (Mw(PSS) = 75.6 kDa) within PSS/PDADMA (Mw(PDADMA) = 72.1 kDa) multilayers is probed while annealing in 1 M NaCl solution at different temperatures. The observed diffusion could not be described by a simple diffusion model. Instead, two different PSS fractions (one mobile and one almost immobile, i.e. different diffusion constants) are the simplest model to describe the time dependence of the scattering length density profiles. Increasing the annealing temperatures (20 - 50 °C) increases the diffusion constant of both the fast and slow PSS fraction. Additionally, the fraction of fast PSS molecules is increased. We suggest that an immobile or nearly immobile fraction of polyelectrolytes is always present when the polymer length is beyond the entanglement limit and the sticky reptation model fails.

CPP 13.4 Tue 10:30 H38

Ratcheting charged polymers through symmetric nanopores using pulsed fields: Designing a low pass filter for concentrating DNA — •Le Qiao and Gary W. Slater — Department of Physics, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

Size-based separation of DNA molecules is crucial for molecular analyses such as genome sequencing. To date, gel electrophoresis is the most commonly used separation method in the laboratory. However, due to poor resolution for larger molecules and difficult sample recovery, it cannot meet the goal of bulk separation. Alternatively, micro/nanofluidics offers a relatively inexpensive, label-free, and continuous separation with high throughput. In this talk, I will present a new proof-of-concept idea for the separation of DNA by contour length using a nanofluidic ratchet by combining nanopore translocation and pulsed fields. Using Langevin dynamics simulations, we show that it is possible to design pulsed fields to ratchet semiflexible molecules such that only short chains are successfully translocated, effectively turning the nanopore process into a molecular low-pass filter. The process itself can be performed with many pores in parallel, and it is possible to integrate it directly into nanopore sequencing devices, increasing its potential utility.

CPP 13.5 Tue 10:45 H38

Tuning water-in-salt electrolytes: impact of concentration and anion structure on local and long-ranged dynamics probed by NMR — •Dominik Gappa, Elisa Steinrücken, Manuel Becher, and Michael Vogel — TU Darmstadt, Institut für Physik kondensierter Materie, Darmstadt, Germany

Water-in-salt electrolytes (WiSE) are highly concentrated aqueous solutions of (Li-)salts. Newly developed WiSE, as they are nonflammable, nontoxic, have a high lithium-ion density and a wide electrochemical stability window (ESW), are promising materials for applications as lithium-ion electrolytes. Due the high amount of the solute and, thus, strong electrostatic interactions between the components they show complex molecular dynamics. A full understanding of interaction mechanism, e.g. the impact of the concentration and anion structure on the dynamics is still elusive. We investigate LiTFSI, which has a wide ESW for different salt concentrations in water. In particular, we exploit the isotope selectivity of Nuclear Magnetic Resonance (NMR) to observe the behavior of the constituents of LiTFSI-H_2O mixtures with various concentrations separately via ^{1}H, ^{7}Li and ^{19}F NMR. The anion structure is modified by extending one side group of the originally symmetric TFSI anion, leading to increasingly heterogeneous dynamics. Local dynamics are investigated by spin-lattice relaxation, including field-cycling NMR, and long-ranged transport by diffusion experiments. Rotational correlation times and diffusion coefficients are extracted to scruntinize the validity of the Stokes-Einstein relation.

CPP 13.6 Tue 11:00 H38

Tuning the Electronic and Ionic Thermoelectric Transport Properties in Polymer Electrolytes by Carbon Based Additives — •Maximilian Frank[1] and Jens Pflaum[1,2] — [1]Experimental Physics VI, University of Würzburg, 97074 Würzburg — [2]ZAE Bayern, 97074 Würzburg

Ionic transport constitutes a key process in organic-based electrochemical energy storage media. As such, it also offers intriguing possibilities for the utilization of these materials in thermoelectrics (TE) to recuperate waste heat into electrical power. In this work we present our results on the electrical and thermoelectrical characterization of a methacrylate based solution processable solid polymer electrolyte. By means of impedance spectroscopy over a broad frequency regime from 100 mHz up to 500 kHz and in a technologically relevant temperature range between 263 K and 363 K we investigate the dynamics of charge carriers in the solidified electrolyte. Furthermore, we demonstrate that the electronic and ionic transport properties can be efficiently varied by the ratio between Lithium-salt and carbon-based additives, in this case, carbon nanotubes. Even more, we can reverse the sign of the occurring thermovoltage, which allows for different TE operational modes depending on ambient temperature. A proof-of-concept all organic TEG verifies the functionality of our approach and, thereby, substantiates the potential of mixed ionic and electronic materials for future TE applications.