

## CPP 61: Charged Soft Matter, Ionic Liquids and Polyions II

Time: Thursday 15:00–17:00

Location: ZEU 114

CPP 61.1 Thu 15:00 ZEU 114

**Impact of Momentum Conservation on the Ion Transport Mechanism in Ionic Liquids in and out of Equilibrium** —

•DIDDO DIDDENS<sup>1,2</sup>, VOLKER LESCH<sup>1</sup>, JENS SMIATEK<sup>3</sup>, and ANDREAS HEUER<sup>1,2</sup> — <sup>1</sup>Helmholtz-Institut Münster (IEK-12), Ionics in Energy Storage, Forschungszentrum Jülich GmbH, Corrensstraße 46, 48149 Münster, Germany — <sup>2</sup>Institut für physikalische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 28/30, 48149 Münster, Germany — <sup>3</sup>Institute for Computational Physics, University of Stuttgart, Allmandring 3, 70569 Stuttgart, Germany

Ionic liquids (ILs) are promising electrolyte materials for batteries or supercapacitors, as the enormous number of possible cation-anion combinations allows their fine tuning to match specific demands. We use Molecular Dynamics simulations to get deeper and more systematic insights into the ion transport mechanism in ILs. In particular, we study the correlated motion of the individual ionic species, and demonstrate that momentum conservation plays a crucial role for the overall transport properties, as it constrains the net motion of all ions. Furthermore, we apply strong electric fields to investigate nonlinear contributions to the conductivity.

CPP 61.2 Thu 15:15 ZEU 114

**Molecular Dynamics and Charge Transport in Polymeric Ionic Liquids** —

•FALK FRENZEL<sup>1</sup>, JIAYIN YUAN<sup>2</sup>, PIA BORCHERT<sup>3</sup>, VERONICA STREHMEL<sup>3</sup>, and FRIEDRICH KREMER<sup>1</sup> — <sup>1</sup>Universität Leipzig — <sup>2</sup>MPI Potsdam - Golm — <sup>3</sup>Hochschule Niederrhein Krefeld

After a remarkable evolution over the last 30 years, nowadays Ionic Liquids (ILs) play an essential role in a wide variety of application areas, as in chemical industry, medicine, and even space technology. However, their low viscosity often excludes them as macroscopic stable components, for instance, in battery electrolytes or gas separator membranes. In order to overcome this constraint (and to satisfy the processing industry) the outstanding features of neat ILs are combined with the well controllable macroscopic properties of polymers, which leads to a novel class of materials known as Polymeric Ionic Liquids (PILs). Although PILs have already demonstrated remarkable performance in electrochemical devices (as in dye-sensitized solar-cells, actuators, or field effect transistors), most fundamental properties are basically not yet understood. In the current study, the chemical structure of PILs is systematically varied and, on the other hand, the measurement techniques of Broadband Dielectric Spectroscopy (BDS), Transmission Electron Microscopy (TEM) as well as Differential Scanning (DSC) and AC-Chip Calorimetry are strategically employed. Hence, one is able to investigate the underlying charge transport mechanism(s), molecular dynamics, polarization effects, and mesoscopic structures in PILs in detail.

CPP 61.3 Thu 15:30 ZEU 114

**Surface composition of a binary system "Ionic Liquid/Lithium Salt", investigated by photoelectron spectroscopy** —

•FABIAN ULLMANN<sup>1</sup>, ANNA DIMITROVA<sup>1</sup>, MARCEL HIMMERLICH<sup>1</sup>, OLIVER HÖFFT<sup>2</sup>, FRANK ENDRES<sup>2</sup>, and STEFAN KRISCHOK<sup>1</sup> — <sup>1</sup>Institut für Physik & IMN MacroNano, Technische Universität Ilmenau, Germany — <sup>2</sup>Institut für Elektrochemie, Technische Universität Clausthal, Germany

Since a decade, the binary systems Ionic-Liquids (ILs)/lithium-salt are widely used media in electrochemistry. They were shown to be an important component in electrolytes for Li-ion batteries, and it is already demonstrated that a number of refractory metals are successfully deposited in ILs only in the presence of Li<sup>+</sup>. In order to control the electrochemical processes, an understanding of molecular and ionic interactions, which occur prior the electrochemical reduction, is required and the influence of side reactions of the electrolyte with the ambient atmosphere has to be known. To this end Photoelectron spectroscopy in ultra-high vacuum (UHV) is a powerful tool, being accessible to the very low vapor pressure of many ILs. In this study we use two ionic liquids with a common anionic part: [Py1,4][Tf2N] and [EMIm][Tf2N], in which Li[Tf2N] was dissolved in different quantities. The surface composition of these binary mixtures was studied both (i) for samples handled and transported to the UHV chamber solely under inert atmosphere and (ii) for those exposed to air before introducing them into the measurement system.

CPP 61.4 Thu 15:45 ZEU 114

**Improving the Lithium Ion Transport in Polymer Electrolytes by Functionalized Ionic-Liquid Additives** —

DIDDO DIDDENS<sup>1,2</sup>, VOLKER LESCH<sup>1</sup>, and •ANDREAS HEUER<sup>1,2</sup> — <sup>1</sup>Helmholtz-Institut Münster (IEK-12), Ionics in Energy Storage, Forschungszentrum Jülich GmbH, Corrensstraße 46, 48149 Münster, Germany — <sup>2</sup>Institut für physikalische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 28/30, 48149 Münster, Germany

Polymer electrolytes consist of a salt dissolved in an amorphous polymer matrix, resulting in mechanically stable and flexible ion conductors. Unfortunately, their conductivity is too low for their use in modern energy storages. To overcome this deficiency, the addition of a low-molecular additive such as an ionic liquid (IL) has been proposed, however, the resulting enhancement is rather modest. Our recent work [1] demonstrated that this stems from the fact that the lithium ions remain coordinated to the slow polymer chains, which move only slightly faster due to the plasticization by the IL. To decouple the lithium ions from the macromolecular host, the use of a functionalized IL with chemically tethered oligomer chains that directly coordinate to the lithium ions has been suggested. We employ Molecular Dynamics simulations to investigate the lithium ion transport mechanism in these improved materials, and compare the results to conventional polymer electrolytes within the framework of our previously developed Rouse-based model [1].

[1] D. Diddens, A. Heuer, *ACS Macro Lett.*, **2013**, 2(4):322-326

CPP 61.5 Thu 16:00 ZEU 114

**<sup>1</sup>H and <sup>7</sup>Li NMR Diffusion and Relaxation measurements of PPG-LiClO<sub>4</sub> polymer electrolytes** —

•SIMON BECKER and MICHAEL VOGEL — Institut für Festkörperphysik, TU Darmstadt, Germany

Polymer electrolytes have been studied since the 1970s as applications for electrical devices because of low costs and mechanical flexibility. To understand effects of polymer-ion couplings on the charge transport in these materials, we use <sup>1</sup>H and <sup>7</sup>Li NMR. Moreover, we employ relaxometry and diffusometry methods to investigate dynamics on local and mesoscopic scales, respectively. We focus on mixtures of poly(propylene) glycol with lithium perchlorate in various concentrations. For these samples <sup>1</sup>H and <sup>7</sup>Li relaxation measurements revealed a strong slow down of segmental motion and ion dynamics with increasing salt concentration. In particular a linear relation between the position of the temperature-dependent <sup>1</sup>H T<sub>1</sub>-minimum and the ion:monomer fraction was observed for the polymer backbone protons. The methyl group spin-lattice relaxation was unaffected by the salt content. The diffusion measurements showed a VFT behaviour of the polymer with reduced diffusivity and fragility for high salt concentrations.

CPP 61.6 Thu 16:15 ZEU 114

**Conductivity Enhancement in Plastic Crystals** —

•DANIEL REUTER, KORBINIAN GEIRHOS, PETER LUNKENHEIMER, and ALOIS LOIDL — Experimental Physics V, University of Augsburg, Germany

Solid-state electrolytes for usage in lithium-ion batteries offer various advantages compared to their liquid counterparts. These are, e.g., design flexibility and higher safety [1]. Plastic crystals (PC) are promising candidates for such solid-state electrolytes. The molecules in a PC are ordered on a regular crystalline lattice while still exhibiting rotational motion. This rotational motion is believed to support ionic mobility in these materials. Interestingly, the ionic conductivity of the PC succinonitrile can be strongly enhanced by doping with ions [2] and admixing molecules [3]. This conductivity enhancement strongly depends on type of dopant and admixed molecule, which opens up a new research field on PCs. In this contribution, we provide dielectric and conductivity data for various mixed plastic-crystalline systems with ion addition.

[1] J. Motavalli, *Nature* **526**, 96 (2015). [2] P. Alarco *et al.*, *Nature* **3**, 476 (2004). [3] K. Geirhos *et al.*, *J. Chem. Phys.* **143**, 081101 (2015).

CPP 61.7 Thu 16:30 ZEU 114

**Study of electrolyte structure and dynamics in Li-S batteries using molecular dynamics simulations with charge-scaling** —

•CHANBUM PARK<sup>1,2</sup> and JOACHIM DZUBIELLA<sup>1,2</sup> — <sup>1</sup>Helmholtz-

Zentrum Berlin for materials and energy, 14109 Berlin, Germany —  
<sup>2</sup>Department of Physics, Humboldt-University of Berlin, 12489 Berlin, Germany

In the recent years, fundamental studies and the development of rechargeable batteries have been focused mostly on the design of cathode materials. Meanwhile, it has become clear that the role of electrolytes are important to improve the current batteries' performance. Molecular dynamics simulations are a good tool to investigate solubility, solvation and transport properties in batteries. Classical molecular dynamics simulations with non-polarizable force fields are able to produce physical properties and commonly used in physics and chemistry. Yet, the non-polarizable force fields simulations become problematic in low/non-polar solvents due to the fixed point charges. Leontyev et al, suggested molecular dynamics in electronic continuum (MDEC) to avoid this shortcoming of the non-polarizable force fields by scaling the ionic charges. In this study, molecular dynamics simulations with the MDEC approach to investigate the mixture of DME/DIOX with two lithium salts, lithium nitrate and lithium bistrifluoromethanesulfonamide (LiTFSI) are performed. Physical properties such as radial distribution function, coordination number, diffusion coefficient and conductivity are examined. In addition, the transport properties in pore structures and the effects of confinement are discussed.

CPP 61.8 Thu 16:45 ZEU 114

**A lattice model to describe lithium ion batteries: insights from Monte Carlo simulations** — ●ALINA WETTSTEIN, OLIVER RUBNER, and ANDREAS HEUER — Institut für Physikalische Chemie, Corrensstraße 28-30, 48149 Münster, Deutschland

Numerous theoretical models have been developed in order to unravel the complex processes which occur in battery electrodes and electrolytes.

While some approaches account for molecular details by employing quantum chemical, molecular dynamics or continuum Monte Carlo calculations, other methods chose a macroscopic ansatz describing the battery cell as a whole system.

Here we present a lattice Monte Carlo (MC) model which seeks to bridge this gap of time and length scales by incorporating molecular and macroscopic parameters. Our MC model is designed as a modular system, which includes the internal electrochemical processes as well as the particle motion given the relevant interactions and rates within a cell. We study how to compute the major electrical properties of a battery, such as voltage and capacity, with a minimum input of outer parameters and test the influence of molecular properties, for example activation barriers, from MD simulations. With the help of this simplified, but highly flexible approach it is possible to further understand the basic principles of Li-batteries.