

CPP 44: Liquids and Ionic Liquids

Time: Thursday 9:30–10:45

Location: H45

Topical Talk

CPP 44.1 Thu 9:30 H45

Glassy dynamics and charge transport in ionic liquids — ●FRIEDRICH KREMER, JOSHUA SANGORO, CIPRIAN IACOB, and JÖRG KÄRGER — Institute of Experimental Physics I, University of Leipzig, Linnéstr. 5, 04103, Leipzig, Germany

Charge transport and glassy dynamics in a variety of glass-forming ionic liquids (ILs) are investigated in a wide frequency and temperature range by means of Broadband Dielectric Spectroscopy (BDS), Pulsed Field Gradient Nuclear Magnetic Resonance (PFG NMR), ac Calorimetry, Differential Scanning Calorimetry and Rheology. The dielectric spectra are dominated - on the low-frequency side - by electrode polarization effects while, for higher frequencies, charge transport in a disordered matrix is the underlying physical mechanism. While the absolute values of dc conductivity and viscosity vary over more than 11 decades with temperature and upon systematic structural variation of the ILs, quantitative agreement is found between the characteristic frequency of charge transport and the structural α -relaxation. This is discussed within the framework of the concept of *dynamic glass transition driven hopping* traced back to Einstein, Einstein-Smoluchowski, and Maxwell relations. A novel approach is applied to extract diffusion coefficients from BDS spectra in quantitative agreement with PFG NMR values but in a much broader range. It becomes possible to extract from the dielectric spectra separately the number density and the mobilities of the charge carriers and the type of their thermal activation.

CPP 44.2 Thu 10:00 H45

Determining the dielectric constant of ionic liquids from computer simulations — ●AXEL ARNOLD — ICP, Universität Stuttgart

We present a new method to reliably calculate the static dielectric constant of charged liquid matter from radial distribution functions, as they can be obtained for example from Monte Carlo or Molecular dynamics simulations. We also explain why a direct measurement of the Kirkwood factor of ionic liquids under periodic boundary conditions cannot generate physically meaningful results.

CPP 44.3 Thu 10:15 H45

Changes of the surface electronic structure of [EMIm]Tf₂N room temperature ionic liquid induced by copper ions — ●ANGELA KEPPLER¹, TOMONORI IKARI^{1,2,3}, OLIVER HÖFFT², MARKUS REINMÖLLER¹, WICHARD J. D. BEENKEN¹, FRANK ENDRES², and STEFAN KRISCHOK¹ — ¹Institut für Physik and Insti-

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The influence of Cu on the surface electronic structure of [EMIm]Tf₂N is investigated using photoelectron spectroscopy. Cu⁺ ions are electrochemically dissolved in [EMIm]Tf₂N. An enrichment of Cu in the near surface region of [EMIm]Tf₂N is obtained in XPS results. By comparing the copper containing IL with the neat [EMIm]Tf₂N a modification of the near surface chemical composition is found. The Cu induced change of the cation/anion ratio directly correlates with the amount of Cu detected by XPS. Additionally, this modifies the valence band structure, which was analysed by XPS and UPS. This modification throws some light on the origin of certain valence band structures and will be discussed on the basis of new DFT calculations. The results will be compared with available data obtained in additional experiments like Cu deposited on the liquid directly under UHV conditions and with data from other ionic liquids ([BMP]Tf₂N and [BMIm]dca).

CPP 44.4 Thu 10:30 H45

DFT-Analysis of Core Levels from Room-temperature Ionic Liquids — ●MARKUS REINMÖLLER¹, ANGELA KEPPLER¹, TOMONORI IKARI^{1,2}, STEFAN KRISCHOK¹, and WICHARD J. D. BEENKEN¹ — ¹Institut für Physik and Institut für Mikro- und Nanotechnologien, TU Ilmenau, P.O. Box 100 565, 98684 Ilmenau, Germany — ²Ube National College of Technology, Department of Electrical Engineering, 2-14-1 Tokiwadai, Ube, Yamaguchi 755-8555, Japan

We performed quantum-chemical calculations by means of density functional theory (DFT) on single ion pairs from imidazolium-based ionic liquids. Thereby we varied the alkyl-chains attached to the imidazolium cation, e.g. from ethyl to octyl at the 1-position, as well as the anion from small like Cl⁻, Br⁻ and BF₄⁻ to more complex like Tf₂N⁻.

By means of the calculated density of states (DOS) projected to the contributions of single atoms, we could directly correlate our theoretical results to experimental XPS data [1], in particular the chemical shifts and splittings of the carbon and nitrogen 1s core level emission.

[1] T. Ikari, A. Keppler, M. Reinmöller, W. J. D. Beenken, S. Krischok, M. Marschewski, W. Maus-Friedrichs, O. Höfft, F. Endres, submitted to e-Journal of Surface Science and Nanotechnology, 2009.