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Temperature dependent study of the local structure of bromine ions in polymerized ionic liquids

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Understanding the structural foundation governing the charge transport is the key for any rational design of electrochemical materials. In this respect, amorphous conductors such as ionic liquids (ILs) and polymer electrolytes are well investigated. At variance with other materials, the polymerized ILs (PolyILs) are prepared through direct covalent bonding of functional monomers containing IL fragments, hence combining the benefits of ILs in terms of high charge density with those of polymers in terms of mechanical stability.
In a recent work the ionic diffusivity of several PolyILs was investigated by means of dielectric spectroscopy combined with nuclear magnetic resonance and differential scanning calorimetry (C. Gainaru et al., J. Phys. Chem. B 120, 2016). Based on the results, we propose a new approach to estimate single-ion diffusivity from the conductivity relaxation by connecting the elementary diffusion step of the ions with structural details.
In order to probe our estimates, we performed EXAFS experiments at beamline BL10 of DELTA and P64 of PETRA III at the Br^- K-edge on monomer and polymer ILs consisting of an imidazolium ring as cation and bromine as anion to reveal temperature-induced changes in bromine's local coordination and connect it to the ionic diffusivity. The measured spectra exhibit major structural differences between the two types of ILs, an exciting result which opens new venues for the understanding of charge transport in concentrated electrolytes.

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