

Charge Transport in Confined Ionic Liquids

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1. Introduction

Nanopores have a great potential for use in drug delivery, nano-fluidic transistors, DNA translocation, catalysis, sensors for chemical agents, nanobatteries, supercapacitors, templates for nanoparticle self-assembly as well as in fundamental research. These applications require in-depth understanding of the motion of molecules or charge carriers inside the pores. We present studies of charge transport in imidazolium-based ionic liquids (ILs) in oxidized nanoporous Si membranes (with average pore diameters: 7.5, 9.5 and 10.4nm) - prepared by electrochemical etching of (100) p-type Si - in a wide frequency and temperature range by a combination of Broadband Dielectric Spectroscopy (BDS) and Pulsed Field Gradient Nuclear Magnetic Resonance (PFG NMR) [1-3].

2. Experimental results

The dielectric spectra are interpreted in terms of hopping of charge carriers over spatially randomly varying energy barriers and results are given in the Fig. 1. The real part of the conductivity σ' in the intermediate frequencies exhibits a plateau, whose value yields the dc conductivity, σ_0 . The decrease observed at lower frequencies is known to be due to electrode polarisation. At higher frequencies, dispersion sets in at a frequency corresponding to the characteristic rate ω_c (which is attributed to the cross-over from diffusive to sub-diffusive dynamics) and σ' shows power-law dependence (inset Fig.1).

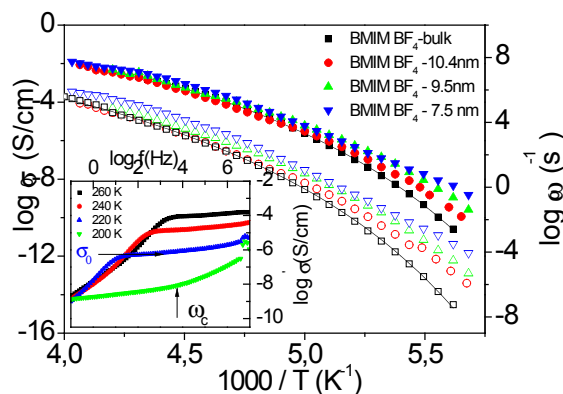


Fig. 1: Temperature dependence of dc-conductivity $\sigma_0(T)$ for bulk BMIM BF₄ and silica nanopores with different pore sizes filled with BMIM BF₄ (denoted by empty symbols) and the characteristic rate of charge transport ω_c (filled symbols). Bulk BMIM BF₄ fits based on the VFT equation are included. Inset: temperature dependence of real part of conductivity σ' as a function of frequency.

By applying the Einstein-Smoluchowski relations to the dielectric spectra, diffusion coefficients are obtained ($D=\lambda^2\omega_c/2$) in quantitative agreement with independent PFG NMR measurements (Fig.2).

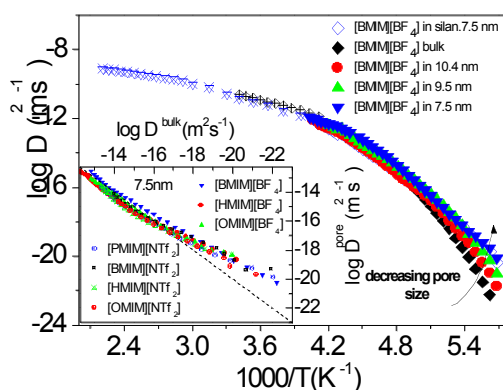


Fig.2 Diffusion coefficients determined by applying the Einstein-Smoluchowski equation to the dielectric spectra of BMIM BF_4 bulk and in different pore sizes. The crossed symbols represent the experimental diffusion coefficients using PFG NMR which are in a good agreement with BDS measurements. Inset: Diffusion coefficients of BF_4^- and NTf_2^- based ionic liquids in 7.5 nm silica nanopores versus bulk diffusion coefficients. Arbitrary dotted line represents 1:1 ratio between diffusion coefficients in pores and in bulk.

At higher temperatures, the diffusion coefficients of the confined and bulk ionic liquids are identical for all pore sizes while ILs are observed to diffuse faster in comparison to their bulk value at lower temperatures. The discussion is conducted with respect to the interplay between the dynamic glass transition and charge transport in ILs.

3. Conclusions

Charge transport in BF_4^- and NTf_2^- based imidazolium ILs which are physically confined into different nanopores is studied by a combination of BDS and PFG NMR. A systematic variation of the pore sizes (7.5nm, 9.5nm and 10.4nm) results in significant changes in the quantities corresponding to glassy dynamics and charge transport processes. Applying the Einstein-Smoluchowski relation to the dielectric spectra, diffusion coefficients in agreement with PFG NMR measurements are obtained. The results are discussed with respect to the ion-ion correlation responsible for changing in the density of ILs at lower temperatures.

4. References

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