diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Molecular Dynamics of Ionic Liquids Confined in Solid Silica Matrix for Lithium Batteries

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(received 15 July 2008, accepted 27 January)

Abstract

We present the first results of the magnetic field dependence of the longitudinal nuclear magnetic relaxation of anion-cation pair of ionic liquids (Li^+-ionogels) confined within a silica-like mesoporous matrices designed for lithium batteries. These results are in favour of a very-correlated dynamical motion of the anion-cation pair within the solid and disordered silica matrix.

Keywords

Ionic liquids, Lithium Batteries, Longitudinal nuclear relaxation, Field cycling relaxometry, Confinement

1. Introduction

Ionic liquids are known for their high ionic conductivity and their wide electrochemical potentiality. They have recently been used as electrolytes in solar and fuel cells [1, 2] and lithium batteries [3]. For such applications, these ionic liquids have been confined in a solid matrix [4, 5]. However, the molecular dynamics of these liquid-like ions within a disordered solid matrix is still unknown. Here, we choose the (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) amide) [BMI][TFSI] as an anion-cation pair of ionic liquid (Li^+-ionogels) confined within a silica-like mesoporous matrices made by a sol-gel route from hydrophobic methyl groups precursors [4, 5]. We present here, for the first time, the nuclear magnetic relaxation dispersion (NMRD) of the confined proton-bearing cation [BMI] in a large range of temperatures. One obtains almost similar NMRD data for the fluor-bearing anion [TFSI]. Several dynamical parameters have been determined from these proton and fluor NMRD such as: translational correlation time, activation energy as well as a surface diffusion coefficient. These first results are in favour of a very-correlated dynamical motion of the anion-cation pair within the solid and disordered silica matrix.

2. Experiments

2.1. Proton and Fluor frequency dependences of nuclear magnetic relaxation dispersion at various temperatures

In a first step, we have measured the proton nuclear magnetic relaxation dispersion (NMRD) of the confined proton-bearing cation [BMI] in a large range of temperatures (Fig. 1). The frequency dependence of $1/T_1$ behaves as a power law, $1/T_1 \sim \omega^{-1/2}$, over more than three orders of magnitude and tends to a plateau at low frequency. This suggests a very slow decay of the intramolecular dipolar fluctuations of this confined cation at proximity of the flat pore surface. Such a power law remains over a very large range of temperature (2°C-90°C). This suggests a translational diffusion process at proximity of the flat pore surface up to a point where all the dipolar correlations disappear. The slight but systematic deviations from such a power law, observed at high frequency for some temperatures, does not change the conclusion given above.

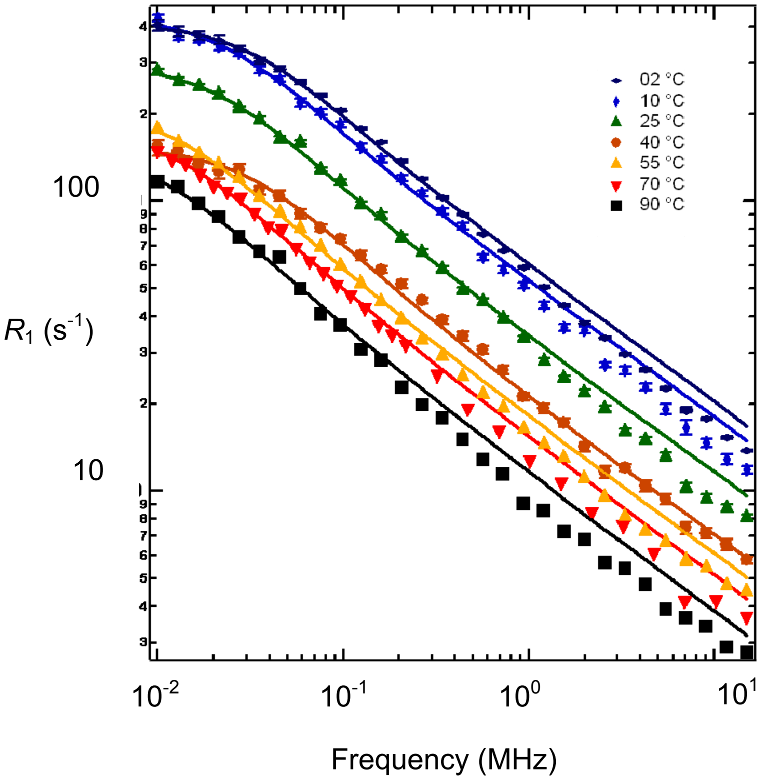

Fig. 1 Logaritmic plot of the frequency dependencies of the proton nuclear magnetic relaxation dispersion of the confined proton-bearing cation [BMI] in solid silica matrix at various temperatures. The continuous lines are the best fits obtained with the theoretical model outlined in the text [ref. 6].

3. Discussions

We have interpreted all the data with an original model that introduces two correlation times: a translational correlation time τ_m for the surface diffusion and a time of residence τ_S over which the ionic liquid stays correlated with the solid surface [6]. These two dynamical

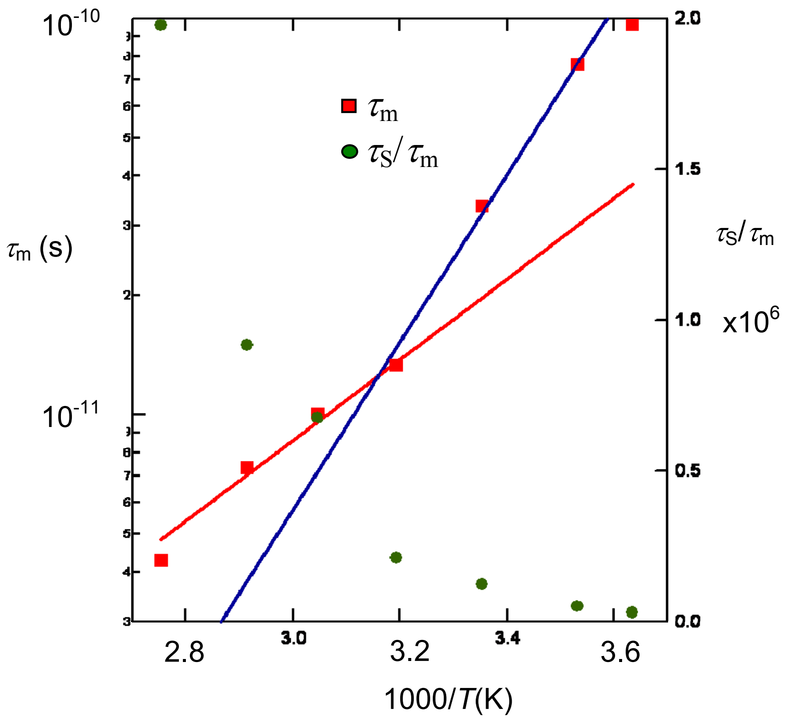

Fig. 2. Arrhenius plot representing the temperature dependences of the translational correlation time τ_m and the ratio τ_S/τ_m for confined proton-bearing cation [BMI] in solid silica matrix. The slopes of the two continuous lines give the activation energies of 4.8 and 10 Kcal/mol at low and high temperatures, respectively.

parameters have been determined from the proton NMRD of Fig. 1 and reported in Fig. 2. on an Arrhenius plot. The ratio τ_S/τ_m describes roughly the number of diffusion steps on the surface or a dynamical surface affinity. We note on Fig. 2 a net modification of the temperature dependence of τ_m and τ_S/τ_m, revealing a change of diffusive regime above 300 K in conformity to recent conductivity measurements [5]. An estimation of the length of persistence associated to an average radius of curvature of the pores has been reached from the cross-over to a frequency independence of $1/T_1$ observed at low frequency. Last, we have observed that the ^{19}F NMRD of the proton-free anion [TFSI] presents a power-law behaviour almost similar to the protons. However there is a single diffusive regime for the anion.

4. Conclusion

Fast field cycling relaxometry has proven useful to obtain dynamical information in favour of a very-correlated dynamical motion of anion-cation pair of ionic liquids (Li^+-ionogels) confined within a silica-like mesoporous matrices designed for lithium batteries.

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