



Full paper/Mémoire

# Multiscale dynamics of $^1\text{H}$ and $^{19}\text{F}$ in confined ionogels for lithium batteries

Dominique Petit<sup>a,\*</sup>, Jean-Pierre Korb<sup>a</sup>, Pierre Levitz<sup>a</sup>, Jean LeBideau<sup>b</sup>, David Brevet<sup>c</sup>

<sup>a</sup> Physique de la matière condensée, CNRS, école polytechnique, 91128 Palaiseau, France

<sup>b</sup> UMR 6502, CNRS, institut des matériaux Jean-Rouxel (IMN), université de Nantes, 2, rue de la Houssinière, BP 32 229, Nantes cedex, France

<sup>c</sup> Chimie moléculaire et organisation des solides, institut Charles-Gerhardt, université Montpellier-2, 34095 Montpellier, France

## ARTICLE INFO

## Article history:

Received 7 May 2009

Accepted after revision 21 August 2009

Available online 28 November 2009

## Keywords:

Ionic liquids

Lithium batteries

Longitudinal nuclear relaxation

Field cycling relaxometry

Confinement

## ABSTRACT

We present the first results of the nuclear magnetic relaxation dispersion (NMRD) of the confined proton-bearing cation (BMI) and fluorine-bearing anion (TFSI) pair of ionic liquids ( $\text{Li}^+$ -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.

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## 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 ( $\text{Li}^+$ -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) (Fig. 1) in a large range of temperatures. One obtains almost similar NMRD data for the fluorine-bearing anion

(TFSI) (Fig. 1). Several dynamical parameters have been determined from these proton and fluorine 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 fluorine frequency dependences of nuclear magnetic relaxation dispersion at various temperatures

We have measured the proton and fluorine nuclear magnetic relaxation dispersion (NMRD) of the confined proton-bearing cation (BMI) and fluorine-bearing anion (TFSI) in a large range of temperatures (2–90 °C) (Fig. 2a and b). These NMRD data were recorded using a fast field cycling FFC NMR spectrometer from Stelar s.r.l., Mede, Italy. We used a fast field cycling sequence to improve the signal to noise, where spins are polarized at 15 MHz and the free-induction decays are recorded following a single 90°

\* Corresponding author.

E-mail address: dpe@pmc.polytechnique.fr (D. Petit).

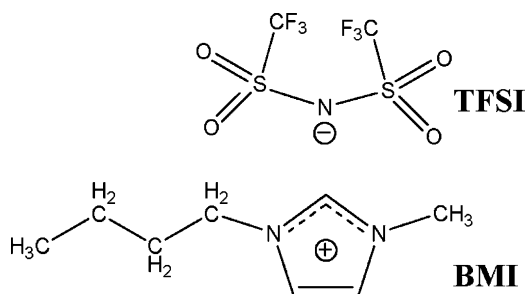


Fig. 1. Molecular structures of the proton-bearing cation (BMI) and fluorine-bearing anion (TFSI).

excitation pulse of 5.8  $\mu\text{s}$  duration applied at 11 MHz. The frequency dependences 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 translational diffusion of this confined cation and anion 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.

The fact that  $^1\text{H}$  and  $^{19}\text{F}$  NMRD have the same frequency behavior over more than three orders of magnitude (Fig. 2) proves that fluctuations at the origin of the relaxation processes are effective on length-scales far above the molecular scale since the NMRD profiles follow this unique power law in a large time range between few ns up to few

$\mu\text{s}$ . It is why the BMI and TFSI NMRD profiles are so similar even if the molecular bonds of the hydrogen and fluorine are so obviously different.

### 3. Discussion

We have interpreted all the NMRD data within an original phenomenological model that describes the nuclear spin-lattice relaxation of proton or fluorine by considering the dipole–dipole interaction modulated by the dynamics in confinement. In this model, we have introduced two correlation times: a translational correlation time  $\tau_m$  for the surface diffusion and a time of residence  $\tau_s$  over which the ionic liquid stays correlated with the solid surface [6]. The main interest of this phenomenological model is to take into account two previous approaches considering either modulation of intramolecular or intermolecular dipolar interactions by bridge statistics [7,8] and explored diffusive volume [9], respectively. The NMRD data are reported in Fig. 2 in the large temperature range studied. The continuous lines on Fig. 2 represent the best fits of the NMRD data achieved with our model. This gives the temperature dependences of the two dynamical parameters reported in Fig. 3.

Considering the temperature dependence of  $\tau_m$  that describes the dynamics of the confined liquid, one notes below 40 °C, similar diffusive behaviours for the cation and anion characterized by an activation energy  $E_{g1} = 10$  kcal/mol and apparently a change of activation energy  $E_{g2} = 4.8$  kcal/mol for the cation above 40 °C in conformity with recent conductivity measurements [1].

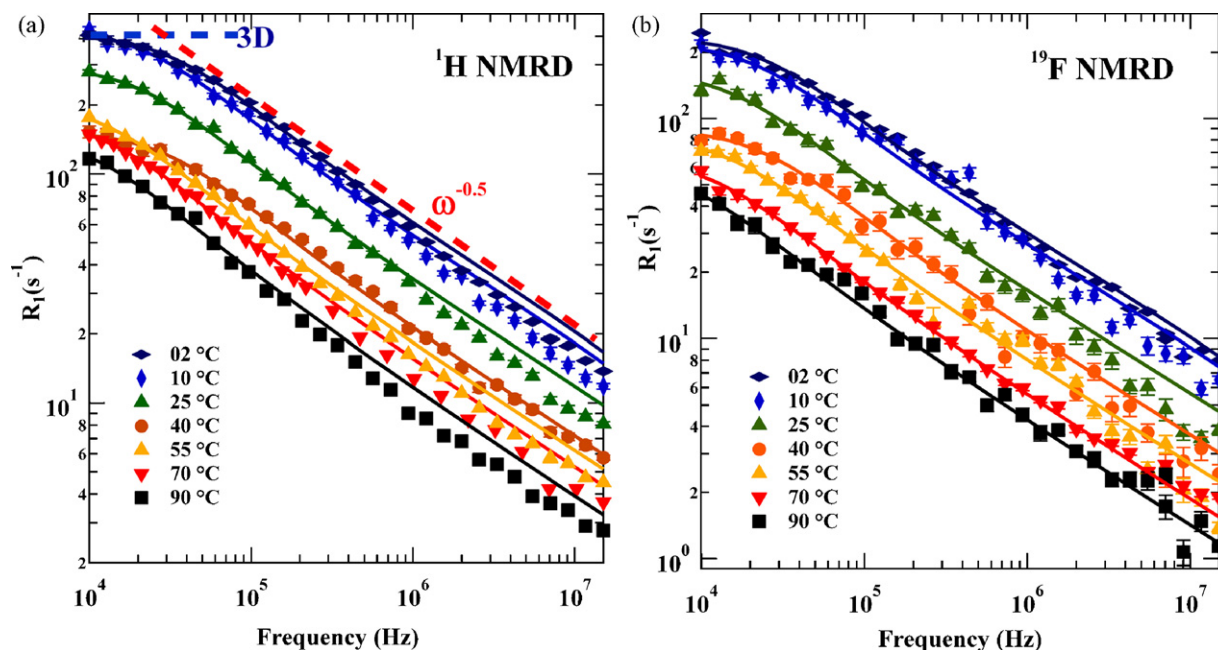


Fig. 2. (a) Logarithmic plot of the frequency dependencies of the proton nuclear magnetic relaxation dispersion of the confined proton-bearing cation (BMI) in solid silica matrix at various temperatures. The continuous lines are the best fits obtained with the theoretical model outlined in the text [6]. (b) Logarithmic plot of the frequency dependencies of the fluorine nuclear magnetic relaxation dispersion of the confined fluorine-bearing anion (TFSI) in solid silica matrix at various temperatures.

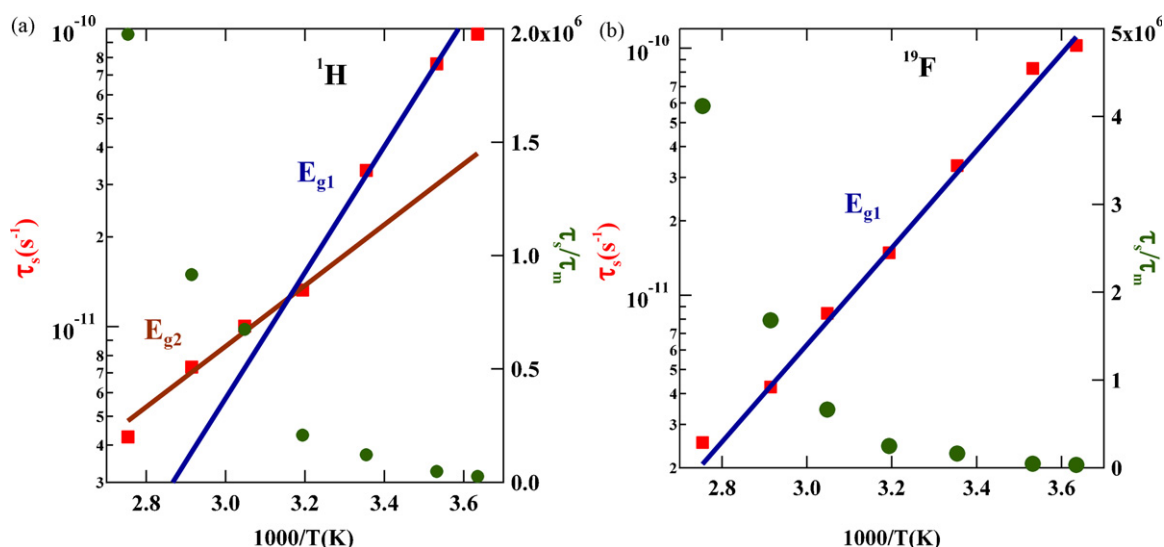


Fig. 3. (a) Arrhenius plot representing the temperature dependencies of the translational correlation time  $\tau_m$  and the ratio  $\tau_s/\tau_m$  for confined proton-bearing cation (BMI) in solid silica matrix. The slopes of the two continuous lines give the activation energies of 10 and 4.8 kcal/mol at low and high temperatures, respectively. (b) Arrhenius plot representing the temperature dependencies of the translational correlation time  $\tau_m$  and the ratio  $\tau_s/\tau_m$  for confined fluorine-bearing anion (TFSI) in solid silica matrix. The slope of the single continuous line gives activation energy of 10 kcal/mol.

The main difference between BMI cation and TFSI anion is the single diffusive regime for the anion of activation  $E_{g1} = 10$  kcal/mol over the whole temperature range. Now, the ratio  $\tau_s/\tau_m$  describes roughly the number of diffusion steps on the surface or a dynamical surface affinity. We note on Fig. 3 an increase of this ratio with temperature. This surprising result may be explained by a diminution of the polarisability when increasing temperature.

#### 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 ( $\text{Li}^+$ -ionogels) confined within a silica-like mesoporous matrix designed for lithium batteries.

#### Acknowledgements

This work has been supported by a grant from the ANR project “LISSIL”.

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