Multi-Nuclear In-Situ Pulsed Gradient Spin Echo (PGSE) NMR Observation of Ion Mobility in Ionic Liquids Used in Battery Technology

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The need to decrease greenhouse gas emissions has strongly increased the need for electric energy storage devices such as rechargeable batteries and super capacitors. Lithium ion batteries currently offer the highest energy density and are therefore of great interest. Due to the limited availability of lithium, interest in sodium-based batteries is also increasing. PGSE NMR offers unique possibilities for investigating such materials [1] [2].

The internal resistance of a lithium Ion battery is strongly dependent on the mobility of the ions involved. In battery development the improvement of the transport properties of the target ions, e.g. by molecular additives, is of upmost importance. PGSE NMR can measure the mobility of different ions separately, independently, and in-situ by measuring the diffusivity of different nuclei, such as ^1H, ^{19}F, and ^7Li. Therefore PGSE NMR is the ideal tool to measure the mobility of the ions.

Using the new broadband diffusion probe (DiffBB) different nuclei can be observed in-situ in full automation.

In order to get a complete picture of the properties of ionic liquids the diffusivity of the different nuclei must be measured over a wide range of temperatures. Currently a temperature range from -40 °C to +150 °C is accessible by the diffBB probe.

Figure 1: Bottom part of a DiffBB probe equipped with a WB adaptor.

Figure 2
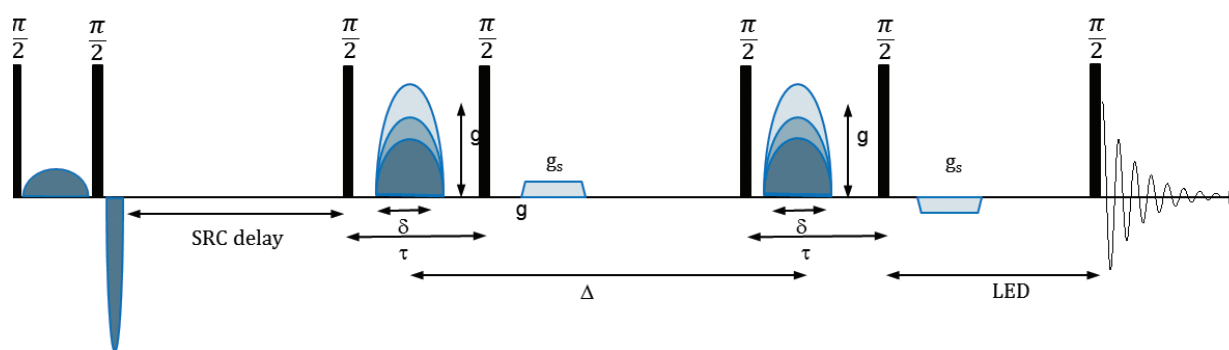
PGSTE pulse sequence with LED, preceded by a spoiler recovery sequence for constant steady state conditions.
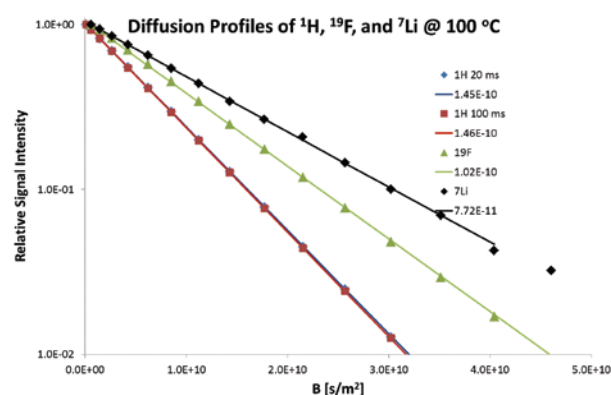
Experimental

As an example of a realistic battery ionic liquid we used a 0.5 molar LiTNf$_2$, often called LiTFSI, dissolved in bmpy NTf$_2$."[3]. In order to avoid disturbances by convection, the sample was filled in a 2 mm capillary tube (id ca. 1.3 mm) placed, axially centered, at the bottom of a regular 5 mm NMR tube.

The experiments were performed on a 500 MHz WB AVANCE III HD spectrometer, using a DiffBB inverse type probe, driven by a GREAT60 gradient amplifier. With this amplifier the probe can reach more than 17 T/m at 60 A. Using water cooling the probe can handle high gradients at a duty cycle of more than 2%. This probe is equipped with a proton channel tunable to ^{19}F with a lock channel attached to the same coil. It also has an X-channel tunable from ^{31}P down to ^{15}N. As the probe has automatic tuning and matching (ATMA) for both channels experiments on 3 nuclei, here ^{1}H, ^{19}F, and ^{7}Li, could be performed at different temperatures in full automation.

The pulse sequence in use was a PGSTE[4] sequence, preceded by a spoiler recovery sequence[5] in order to avoid long waiting times for relaxation. The spoiler recovery delay was set to 1s. The effective gradient pulse length δ was set between 1 ms and 3 ms, the diffusion time Δ between 20 ms and 100 ms. Most experiments were performed at a Δ of 20 ms, except for ^{7}Li at low temperatures, where longer Δ values were required in order to get big enough B values. For ^{1}H two experiments with Δ = 20 ms and Δ = 100 ms were performed at each temperature step in order to prove the lack of convection. At the end of the sequence an LED sequence[6] with an LED delay of 20 ms was added to remove possible eddy current effects.

Figure 3

Diffusion profiles at 100 °C. The ^{1}H were experiments performed at diffusion times of 20 ms and 100 ms are almost identical indicating the absence of convection.

Results and discussion

All experiments show mono-exponential behavior for all nuclei/ions over the whole temperature range (Figures 3 and 4). This indicates the ions are diffusing as single ions or in clusters of the same size.

Experiments on different nuclei can be performed over a wide temperature range with full automation. The experiment using 2 diffusion times, 20 ms and 100 ms, in ^{1}H proved no convection was present (Figure 3).

At low temperature the full gradient strength of a high power diffusion probe is required to investigate x-nuclei, such as ^{7}Li in this example (Figure 4).

The Arrhenius plot in Figure 5 first shows a slightly deviation behavior from Arrhenius' law. Nevertheless, in the first approximation the standard Arrhenius law can be fitted to the data showing almost identical activation energies of 0.43 +- 0.01 eV for the ions carrying the different nuclei.

Conclusions

These experiments were meant to show the possibilities of PGSE diffusion in the field of lithium ion battery research. Particularly the use of the new DiffBB probe facilitates automatic measurements of such substances significantly. The accessible diffusion coefficients could be reduced even further for ^{7}Li using longer diffusion times .

Figure 4

Diffusion Profiles of ^{1}H, ^{19}F, and ^{7}Li @ 0°C
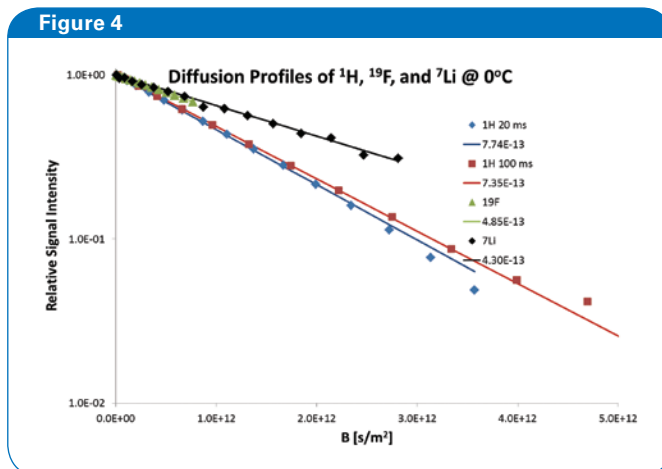
Diffusion profiles at 0 °C. The ^{7}Li experiment uses the full gradient strength showing high gradient strength is absolutely required in the case of X nuclei.

Figure 5
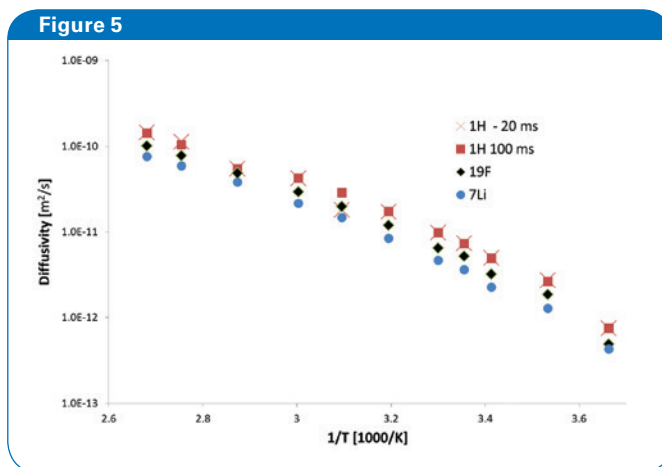
Arrhenius plot of the diffusion coefficients obtained from ^{1}H, ^{19}F, and ^{7}Li over the temperature range of 0 to 100 °C. The activation energy is approximately the same for all ions (0.43 eV)

References

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