



## MAGNETIC RESONANCE FOR BATTERIES RESEARCH AND MANUFACTURING

# Quantifying Ionic Conductivity and Cation Transfer Coefficient in Lithium-ion Battery Electrolytes by Diffusion Ordered NMR Spectroscopy

Sarah Mailhiot Ph.D. , Application Scientist- MR Microscopy , Bruker BioSpin GmbH, Ettlingen, Germany

Antonios Papaioannou Ph.D., Application Scientist-NMR Microscopy and Diffusion, Bruker BioSpin GmbH, Ettlingen, Germany

Innovation with Integrity

### Introduction

The demand for rechargeable batteries is projected with double-digit annual growth rates already till the end of the next decade. Applications such as energy storage in battery electric vehicles (BEV) and large-scale stationary storage are the driving factors of this development. The battery's essential components include the electrodes, a separator membrane, and the liquid electrolyte as a conducting medium. The performance of these batteries is dependent on the electrode material, cycling stability, electrolyte stability, charge/discharge rates, energy density, and electrical conductivity<sup>[1]</sup>. Mobility of the ions and ion diffusion in the electrolyte phase effects the charge/discharge rate, energy density<sup>[2]</sup>, and electrical conductivity<sup>[3]</sup>. To increase the performance of batteries, it is critical to be able to characterize the mobility of ions in the electrolyte. These performance factors will be key for improving the existing electrochemical setup of batteries and to develop the next generation technology. Raw material cost and availability will be limiting factors in this growth projection. Academic and industrial researchers will also need new analytical testing techniques to drive innovation in the global battery market.

### Electrolytes

The most common type of commercial lithium-ion battery is lithium hexafluorophosphate ( $\text{LiPF}_6$ ) salt dissolved in mixtures of carbonates such as ethylene carbonate (EC), dimethyl carbonate (DC), or diethyl carbonate (DEC). One way to evaluate the suitability of an electrolyte is to measure the mobility of the solvent as well as the mobility of the dissolved  $\text{Li}^+$  and  $\text{PF}_6^-$ . The charge transport during both phases of the battery cycle is fundamentally linked to the ion mobility. NMR Diffusion Ordered Spectroscopy helps answer the question: "Does my electrolyte effectively conduct electricity?"

## Diffusion Ordered NMR spectroscopy and Electrical Conductivity

Nuclear Magnetic Resonance (NMR) spectroscopy is a non-destructive technique, using the inherent magnetic properties of specific atomic nuclei to characterize the molecular species in solid-state or in a liquid sample. Diffusion Ordered Spectroscopy (DOSY) is an experimental NMR technique that measures the self-diffusion coefficient,  $D$ , of these molecular species<sup>[3]</sup>. The self-diffusion coefficient is a direct measure of the mobility of the molecular species and has a direct relationship to electrical conductivity,  $\sigma$ , following the Nernst-Einstein relationship,

$$\sigma = \frac{F^2(D_- + D_+)}{RT} \quad (\text{Eq. 1})$$

In equation (1),  $F$  is Faraday's constant,  $D_-$  is the self-diffusion coefficient of the anion,  $D_+$  is the self-diffusion coefficient of the cation,  $R$  is the ideal gas constant, and  $T$  is the temperature. The self-diffusion coefficients of the cation and anion also have a direct relationship with the cation transfer coefficient,  $t_+$ <sup>[4]</sup>.

$$t_+ = \frac{D_+}{D_+ + D_-} \quad (\text{Eq. 2})$$

In the dilute limit for a binary salt mixture such as  $\text{LiPF}_6$ , the cation transfer coefficient is the fraction of total conductivity that is carried by the cation.

## The multi-nuclear AVANCE-400 NMR solution for electrolytes

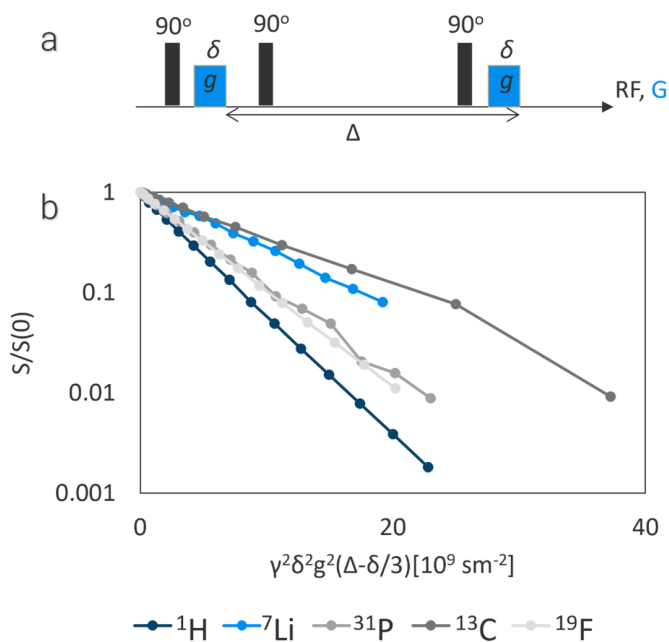
Due to the chemical nature of the electrolytes' components, multi-nuclear NMR spectroscopy can be used to gain insight, quantify, and understand changes in the electrical conductivity of the electrolyte. For example, quantification of species containing  $^1\text{H}$  and  $^{13}\text{C}$  in the solvent can be used to assess the solvent mobility and viscosity. Quantification of the mobility of salt ions containing  $^{19}\text{F}$ ,  $^{31}\text{P}$ , and  $^7\text{Li}$  can be used to calculate the molar ionic conductivity and the cation transfer coefficient. Typically, a dilute binary salt mixture, the order of diffusivities is  $D_{\text{solvent}} > D_+ > D_-$ <sup>[5]</sup>. Other nuclei for next generation battery technologies, such as but not limited to  $^{23}\text{Na}$ , are accessible by this technology as well.

## Quantification of Electrical Conductivity of Liquid Electrolytes

DOSY measurements are made by applying magnetic field gradients<sup>[3]</sup>. In the encoding period, a magnetic field gradient is applied to the spin ensemble which results in a position dependent phase. The spins are then allowed to diffuse for an observation time,  $\Delta$ . During the decoding period, a magnetic field of the opposite magnitude to the encoding period is applied, which cancels out the phase acquired during the encoding period if the spins have not moved. On the contrary, if the spins have moved, the signal attenuates. The signal decay is then described as:

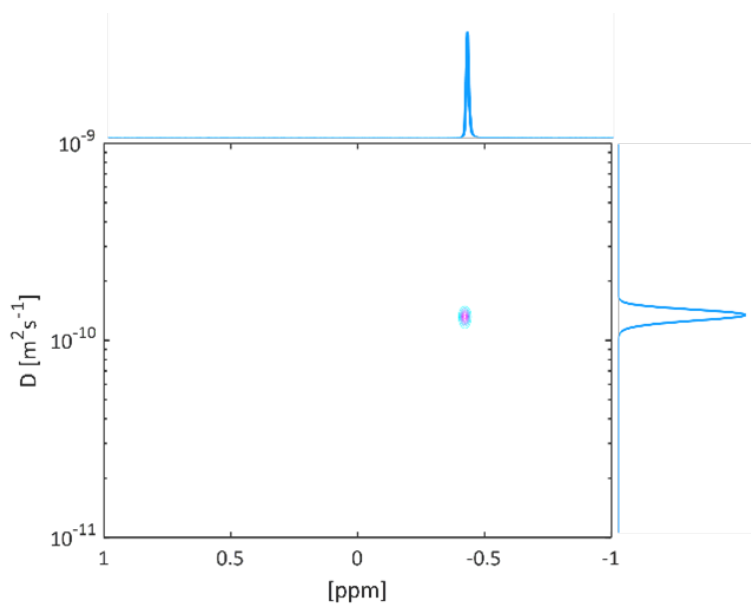
$$S(g^2)/S_0 = \exp\left(-\gamma^2 g^2 \delta^2 D \left(\Delta - \frac{\delta}{3}\right)\right) \quad (\text{Eq. 3})$$

In equation (3),  $\gamma$  is the gyromagnetic ratio and is specific to the nuclei of study,  $g$  is the applied gradient strength,  $\delta$  is the time the gradient is applied, and  $\Delta$  is the diffusion observation time. The experiment is repeated with an incremental increase in  $g$  to acquire a signal decay.



**Figure 1** (a) Pulse program for acquiring DOSY data. (b) Diffusion signal decay for  $^1\text{H}$ ,  $^{13}\text{C}$  nuclei in EC (ethylene carbonate) and DEC (diethyl carbonate) solvent and  $^7\text{Li}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  in  $\text{LiPF}_6$ .

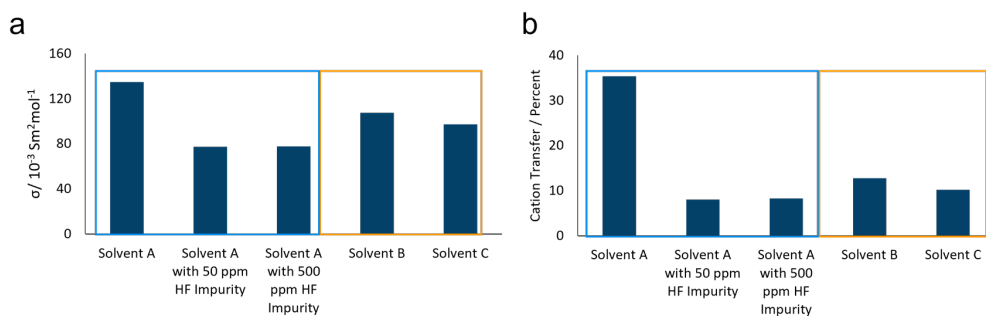
To create a DOSY plot, the signal decay is analysed for all peaks in the spectra and a  $D$  coefficient is fit. A DOSY plot for  $^7\text{Li}$  is shown in Figure 2, however these plots can be made for all nuclei.



**Figure 2**  $^7\text{Li}$  DOSY of Li in  $\text{LiPF}_6$  dissolved in a mixture of carbonates.

Using the diffusion coefficients from the DOSY plots of the anion ( $^{19}\text{F}$ ) and cation ( $^7\text{Li}$ ) in  $\text{LiPF}_6$ , the molar electrical conductivity and cation transfer can be found (Eq 1,2). The electrical conductivity and cation transfer are sensitive to salt, solvent, impurities, and temperature <sup>[6]</sup>.

For further, detailed information about DOSY NMR and its contribution to electrolyte characterization, please see the review paper by A.V. Karatrantos et al. <sup>[1]</sup>.



**Figure 3** (a) Molar electrical conductivity ( $\sigma$ ) and (b) cation transfer ( $t_+$ ) of screened  $\text{LiPF}_6$  as a function of HF concentration as well as solvent mixtures. Measurements were taken at 27° C.

## Conclusion

Developing and optimizing the electrochemistry of existing and new battery designs requires intense cooperation of various analytical testing techniques. Understanding the fundamental performance characteristics of various battery components is an essential baseline prior to assembling first test cells.

Using information from DOSY NMR measurements, the properties of the electrolyte can be optimized in a targeted and efficient manner. It can also help determine the electrolyte contribution to the total performance of the cell. Electrolytes extracted from cycled test cells can also be investigated after the formation process which helps to better understand structural changes.

Overall, this information can shorten the time for formulation optimization, which also shortens time-to-market for new batteries. Applying the most modern analytical testing techniques will lead to a significant competitive advantage in the growing battery market.

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