Application Note 16

# Multinuclear Benchtop NMR for Electrolyte Design

Introduction

Benchtop NMR enhances electrolyte design by enabling rapid and routine measurement of key performance parameters including electrolyte composition, diffusion coefficients of each component, conductivity, transference number and viscosity. Hence, it provides critical data for the design of new electrolyte formulations and optimization of their performance. This application report outlines practical approaches for NMR electrolyte analysis and how the measured parameters can affect performance using examples from lithium battery R&D.

Electrolytes, which consist of anions and cations in a solvent system, are a key component in battery performance. Rechargeable lithium-ion (Li-ion) batteries offer high energy density and have become extremely popular, providing energy storage for electronics, medical devices, and electric vehicles. Current battery technologies use small-molecule liquid organic solvents, such as ethylene carbonate (EC), dimethyl carbonate (DMC), coupled with small Li^+ and hexafluorophosphate ($[PF_6]^-$) ionic species. However, new electrode formulations such as Li -metal, lithiated silicon or lithium sulfur, require new electrolyte chemistries. Optimizing the electrolyte performance delivers improvements in power output, longevity, and safety, making development of new systems a high priority.

To accelerate development of new formulations, quick, convenient analysis methods of multiple properties of the individual components are crucial. Currently, when electrolyte diffusion is measured, electrochemical techniques, such as Potentiostatic or Galvanostatic Intermittent Titration (PITT and GITT) are used. These techniques typically take many hours and are usually only performed within a whole battery or cell, making them inconvenient for rapid analysis of large numbers of potential formulations. In contrast, NMR provides results directly on a small sample of electrolyte in less than an hour in any laboratory quickly, easily, and with only simple sample preparation.

Benchtop NMR quantifies solvent composition, levels of ionic species, and the individual diffusion coefficients of each component. From the NMR data, ionic conductivity, ion transference number, and viscosity changes can be determined. A single X-Pulse broadband benchtop NMR spectrometer provides a complete rapid electrolyte analysis solution. It combines pulsed field gradient hardware with variable temperature operation from 20-60°C, and the ability to monitor all key nuclei within an electrolyte, including ^1H, ^{19}F, ^{13}C, ^{11}B, ^7Li, ^{31}P, and ^{23}Na.

ANODE   **ELECTROLYTE**   **CATHODE**

e⁻ ↑

↓ e⁻

−

+

SEPARATOR ↑

Li SALTS

LiTFSI

Li⁺

F
F—S
F
O=S=O
N
S
O
F
F
F

LiBF₄

F
F—B—F
F   Li⁺

LiPF₆

Li⁺
F   F   F
P
F   F   F
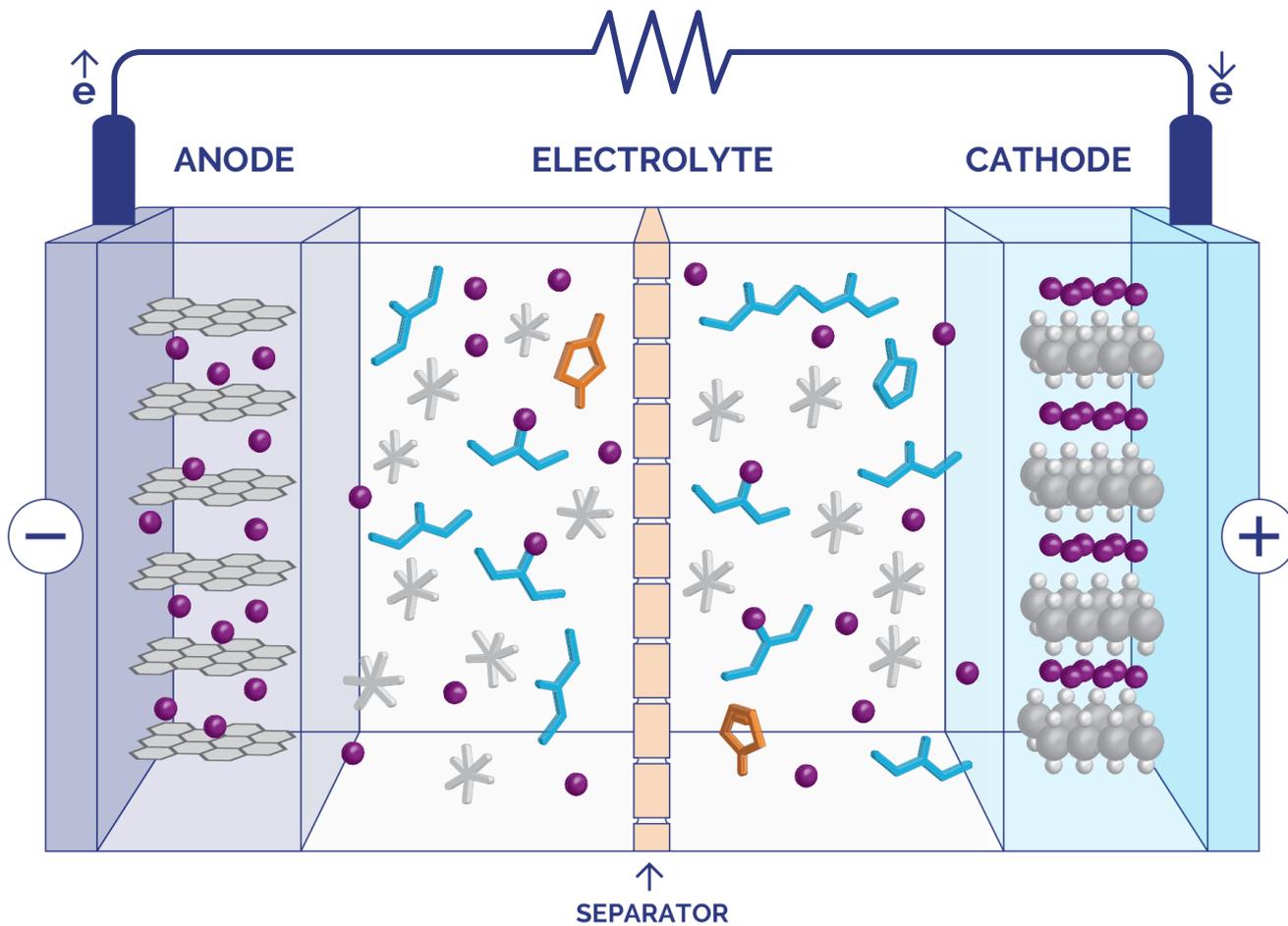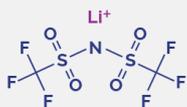
ORGANIC SOLVENTS

EC

PC

DMC

DEC

EMC

ADDITIVES

FEC

F
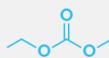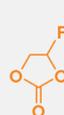
VC

KEY

Graphite structure

Li⁺

LiMO₂ layer structure

Figure 1: Schematic of the major components of a lithium-ion battery, showing electrolyte components, anode, cathode, and separator.

Electrolyte Solvent Analysis

Unlike bulk viscosity measurements, the NMR technique directly measures diffusion of electrolyte components, allowing insight into how changes in the environment affect each one individually, providing critical information for electrolyte design.
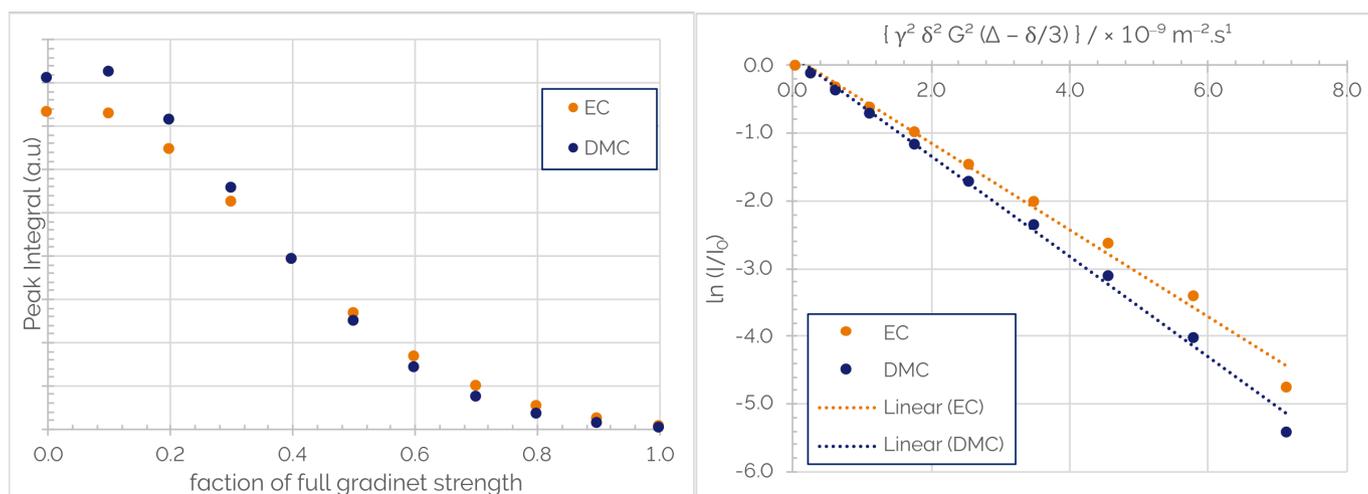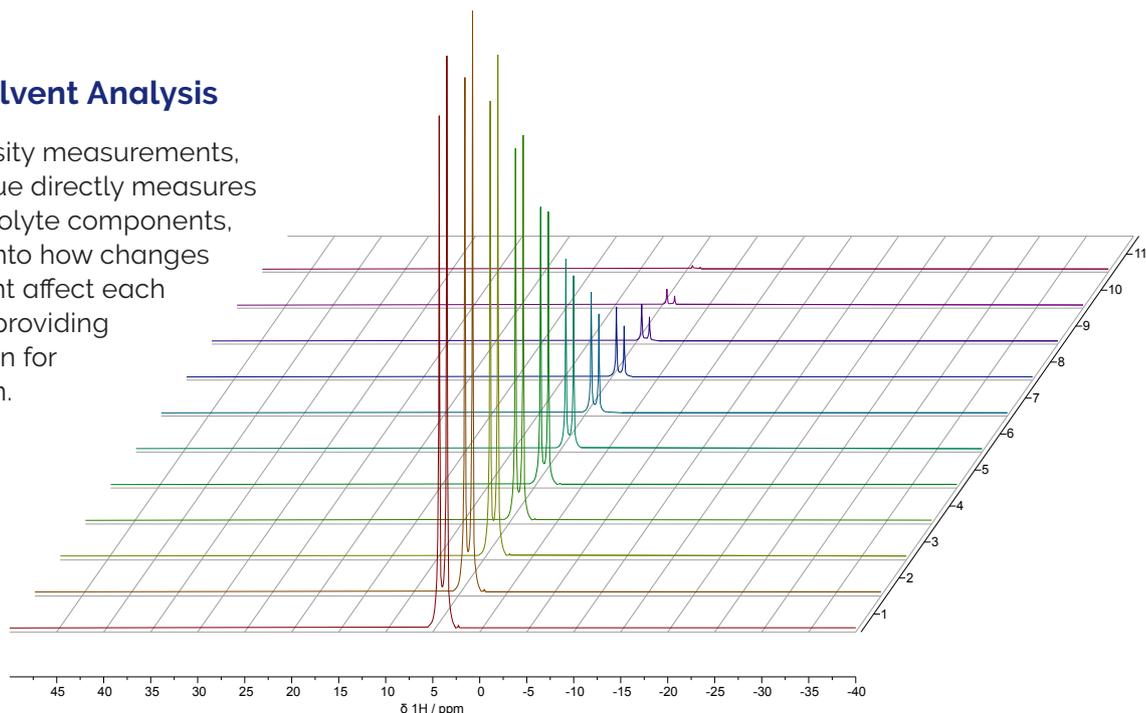

Figure 2: Diffusion measurements for an electrolyte solvent mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). (A) A series of PFGSE spectra at different gradient strengths, showing well-resolved peaks for the two solvent components. (C) Stejskal-Tanner linear plot, which allows simple calculation of diffusion constants for each component, from the slopes of the lines. The excellent linearity of the plots shows the high stability of the instrument and the strong linear response of the gradient amplifier.

Figure 2 shows typical NMR diffusion data obtained using Pulsed Field Gradient Spin Echo (PFGSE) experiments for an electrolyte solvent mixture, consisting of ethylene carbonate (EC) and dimethyl carbonate (DMC), measured at 39.5˚C. The calculated diffusion constants in Table 1 demonstrate that NMR can easily resolve differences in behavior in individual components within a mixed solvent, which can be crucial when trying to understand the interaction between the solvents and ionic species. The "Measuring Diffusion at Different Temperatures Using NMR with Pulsed Field Gradients" application note provides a more detailed description of this NMR diffusion analysis method.

Component	Diffusion constant (D) (m²/s)
Ethylene Carbonate	6.42×10^{-10}
Dimethyl Carbonate	7.38×10^{-10}

Table 1: Diffusion constants for EC and DC, calculated from the PFGSE experiment.

In an ideal system, solvent viscosity can be directly related to the three-dimensional diffusion constant by the Stokes-Einstein equation:

$$D = \frac{k_B T}{6\pi\eta r'_H}$$

where k_B is the Boltzmann constant, T is temperature, r_H' is the radius of the molecular sphere, and η is the viscosity. In real solutions, factors such as temperature and molecular interactions affect individual components in different ways. NMR measures diffusion of individual solvent components, providing more information than bulk viscosity measurements and revealing which specific components of a mixture may be critically affected by changes in composition. Moreover, an X-Pulse spectrometer equipped with the variable temperature feature can measure temperature-dependent performance, allowing evaluation of solvent components under a range of battery operating conditions. This information is key in understanding the mechanisms behind differences in solvent behavior, speeding development of new formulations, therefore saving development time and reducing costs.

Measuring Ionic Properties of Electrolytes

Benchtop NMR provides crucial information beyond simple diffusion analysis of the organic components of battery electrolytes. The multinuclear capabilities of the X-Pulse benchtop NMR allow a single instrument to analyze the behaviour of many common ionic species. From the diffusion constants of the ionic species, the ionic conductivity (σ) and transference number ($t_{+/-}$) is determined.

Conductivity is crucial for lithium-ion batteries, affecting properties such as energy density and speed of charge/discharge cycles (power density). The transference number denotes the fraction of electrical current carried in the electrolyte by an ionic species. Conveniently, both parameters can be determined from self-diffusion constants obtained on an X-Pulse using the Pulsed Field Gradient Spin Echo (PFGSE) experiment on a single electrolyte sample.

The ionic conductivity (σ) can be calculated from the self-diffusion constants of the anionic and cationic species using the Nernst-Einstein relationship:

$$\sigma = \frac{F^2 c (D_+ - D_-)}{RT}$$

where F is the Faraday constant, R is the gas constant, T is the absolute temperature, c is the bulk molar salt concentration, and D_+ and D_- are the self-diffusion constants of the cationic and anionic species, respectively.

Calculating transference numbers is even more straightforward, using the simple equations:

$$t_+ = \frac{D_+}{D_+ + D_-} \text{ and } t_- = \frac{D_-}{D_+ + D_-}$$

where t_+ and t_- are the cationic and anionic transference number, respectively, and D_+ and D_- are the measured diffusion constants for the cation and anion, respectively. A large transference number can reduce concentration polarization of electrolytes during charge–discharge steps, producing higher power density. Optimally, t_+ should be close to 1 for a lithium-ion battery.

As an example, Lithium hexafluorophosphate salt (LiPF$_6$) was studied in three different electrolyte solvents: DMC, a 50:50 mixture of EC and DMC, and propylene carbonate (PC). The PFGSE spectra are shown in Figure 3.
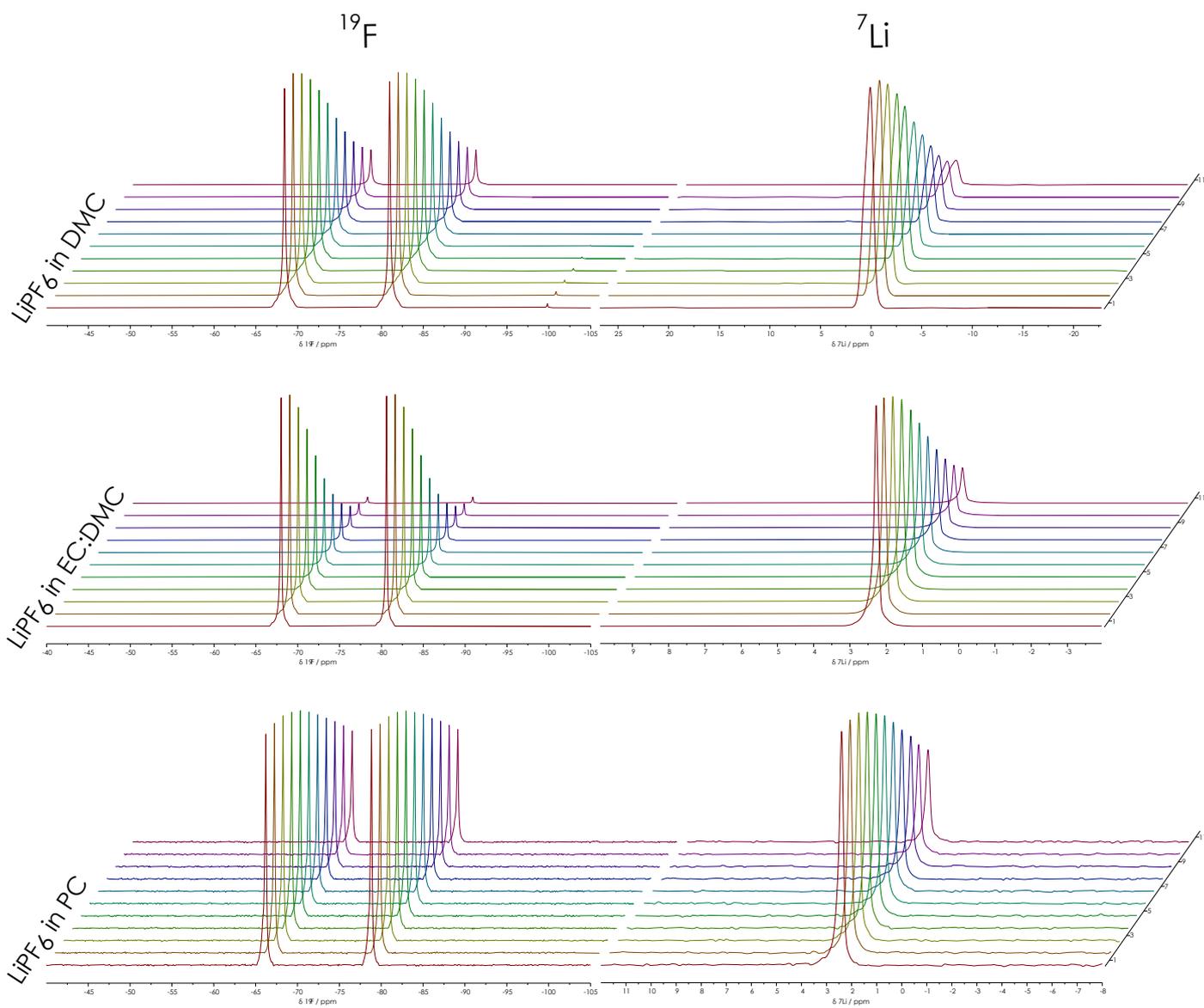

Figure 3: Stacked PFGSE spectra from 10 to 100% of the full gradient strength for LiPF$_6$ in three different alkyl carbonate solvents, measured at 39.5°C.
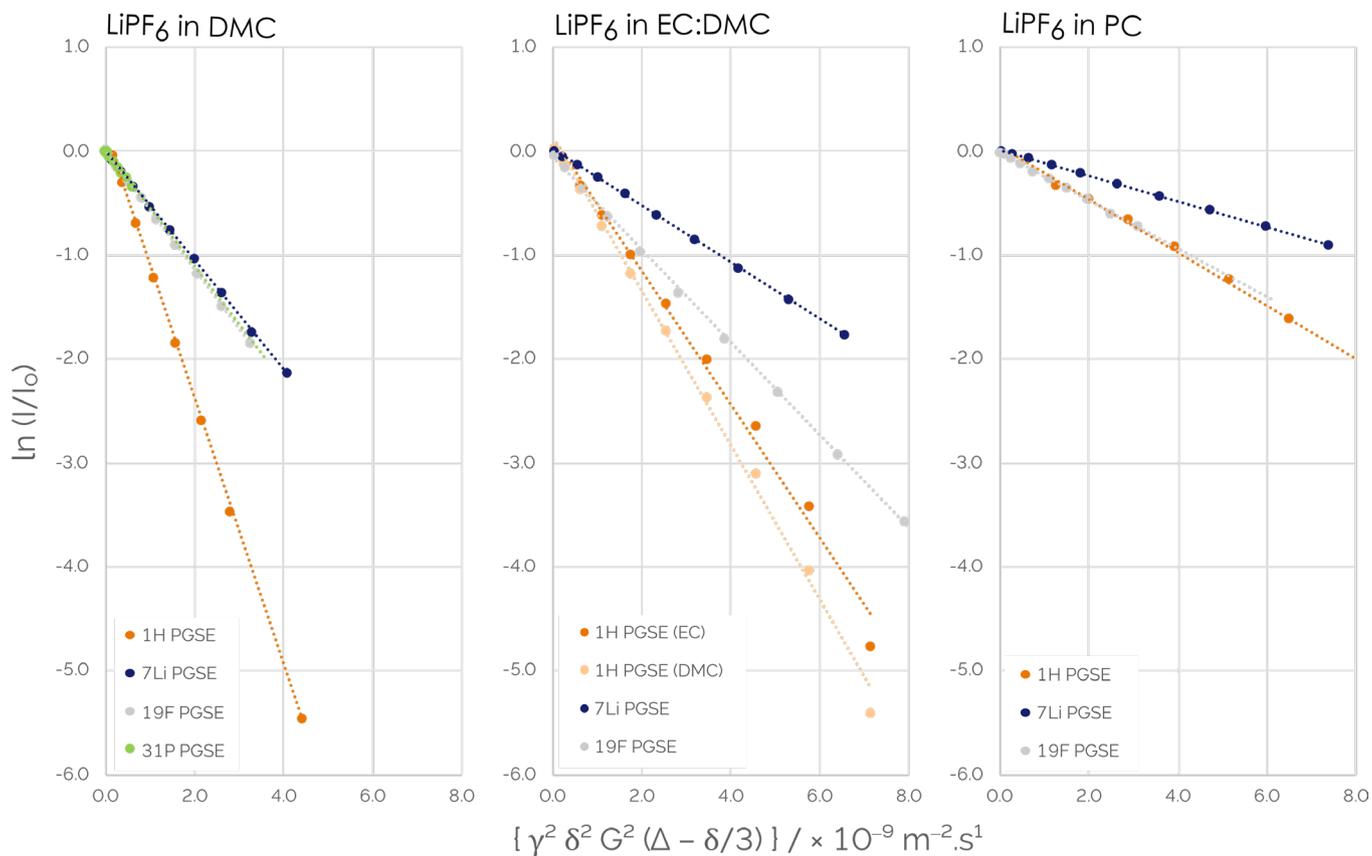
Figure 4: Stejskal-Tanner plots of integrals obtained from PFGSE data of LiPF$_6$ in DMC, 50:50 EC:DMC, and PC. ^{1}H data is shown in dark orange and light orange ^{7}Li data is shown in blue, ^{19}F in gray, and ^{31}P in green. All data were acquired on a single X-Pulse broadband benchtop NMR spectrometer.

Sample	D$_+$, cation	D$_-$, anion	D, solvent	Conductivity	Transference (t$_+$)
	x10^{-10} m^{2}s^{-1}		@ 39.5°C	x10^{-3} Sm^{-1}	
DMC	5.16	5.68 (^{19}F) 5.81 (^{31}P)	12.7	3.91	0.48
EC:DMC	2.74	4.45	6.42 (EC) 7.38 (DMC)	2.54	0.38
PC	1.24	2.30	2.56	1.28	0.35

Table 2: Parameters measured by NMR for three electrolyte systems: LiPF$_6$ in DMC, in 50:50 EC:DMC, and in PC. Diffusion constants were determined for the cation, anion, and solvent, along with conductivity and the cation transference (t$_+$).

Figure 4 reveals the differences in diffusion behavior among components of a single electrolyte solution, as well as differences among the same species in different solvent conditions. Because ^{31}P is part of the same $[PF_6]^-$ ion as ^{19}F, the two should diffuse at the same rate. In fact, the diffusion behaviors were identical within the precision of the method. However, as expected, the diffusion behavior of the smaller Li^+ ion differed significantly from that of ^{19}F in the larger $[PF_6]^-$ ion. In addition, the markedly different quantitative results in Table 2 for the same Li^+ and $[PF_6]^-$ ions in the three solvent systems demonstrate the importance of solvent choice in battery design. Conductivity differed by approximately a factor of three between electrolytes using PC and DMC solvents, while cation transference changed far less. Moreover, the difference in diffusion behavior for DMC as a pure solvent, compared to the 50:50 mixture with EC, demonstrates the effects of environment on solvent molecules.

Conclusion

Benchtop NMR has become a powerful laboratory technique for lithium-ion battery analysis. It quickly and easily distinguishes between the diffusion behavior of different electrolyte solvents, as well as between diffusion of the ionic species and the solvent. Important parameters such as conductivity and ion transference numbers are easily determined from the NMR data. Together, these provide a detailed quantitative analysis of individual components and ultimately of the electrolyte system performance. The X-Pulse broadband benchtop NMR spectrometer therefore provides critical data for electrolyte design in any laboratory environment.

Moreover, other benchtop NMR applications significantly improve quality control and raw materials checking for next generation batteries. More applications notes and case studies can be downloaded at **https://nmr.oxinst.com/batteries**.

If you have any questions about this application note, please contact our experts:
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