

Liquid NMR-Spectroscopy as Powerful Tool for Electrolyte Characterisation

P. Handel¹, C. Stangl¹, M. Schmuck¹, R. Fischer², S. Koller¹

¹VARTA Micro Innovation GmbH, Stremayrgasse 9, A-8010 Graz

²Institute of Inorganic Chemistry, Graz University of Technology, Stremayrgasse 9/V, A-8010 Graz

contact: p.handel@vam-austria.com; +43 316 873 32344

Abstract

The thermal decomposition of conventional lithium-ion battery electrolytes was studied by nuclear magnetic resonance (NMR) spectroscopy at ambient and elevated temperature, respectively. Alkylfluorophosphates and fluoro-

phosphoric acids were identified as main decomposition products. Additionally, NMR-spectroscopy allows the identification and structure elucidation of different electrolyte components.

Introduction

State-of-the-art electrolyte systems of lithium-ion batteries (LIBs) [1] suffer from thermal decomposition, which can be severely increased by traces of protic impurities, most notably water, due to the hydrolysis sensitivity of the P-F bonds of lithium hexafluorophosphate (LiPF₆). [2] In fact, the decomposition of LiPF₆ is favored at higher temperatures leading to the formation of hydrofluoric acid (HF) and

subsequently to further degradation of electrolyte components. [3]

Since most nuclei contained in electrolytes possess a spin quantum number of ½ high resolution nuclear magnetic resonance (NMR) spectroscopy is a powerful tool for structural elucidation of e.g. electrolyte additives and its decomposition products.

Experimental

Samples for NMR-spectroscopy were flame-sealed under reduced pressure in NMR-tubes and afterwards aged at room temperature and 60°C. All flame-sealed tubes contained either a D₂O or C₆D₆-capillary to avoid contamination with deuterated solvents.

¹H-, ¹³C-, ¹⁹F-, and ³¹P-NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer. ¹H- and ¹³C-NMR spectra were referenced to (CH₃)₄Si, ¹⁹F-NMR resonances to CCl₃F and ³¹P-NMR resonances to H₃PO₄.

Fluorinated and phosphorylated decomposition products could be identified via using their chemical shift, coupling constants and multiplicities. A major problem was the precipitation of white solid in the NMR-tubes upon ageing since solids lead to faster relaxation times. The resulting peak broadening worsens the resolution.

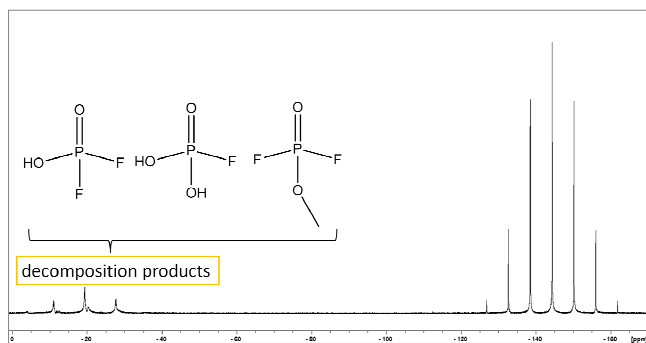


Figure 1: ³¹P-NMR spectrum of 1M LiPF₆ in EC:DMC (1:2, v/v) exposed to 60°C for four weeks. OPF₂OH, OPF(OH)₂ and OPF₂OMe could be identified as thermal decomposition products in the region of -7.99 to -20.34 ppm. The septet at -144.33 ppm corresponds to the conductive salt LiPF₆.

Table 1: List of measured NMR-active nuclei.

nucleus	spin	nat. abundance [%]	γ*	frequency**[MHz]
¹ H	½	99,98	26,75	300,224
¹³ C	½	1,108	6,73	75,499
¹⁹ F	½	100	25,18	282,47
³¹ P	½	100	10,83	121,532

*gyromagnetic ratio [$\times 10^7$ rad T⁻¹ s⁻¹] **at a magnetic field strength of 7,05 T

Beside the identification of decomposition products of LiPF₆, ¹⁹F-NMR is also capable to monitor the presence or changes of fluorinated electrolyte additives like monofluoroethylene carbonate (FEC).

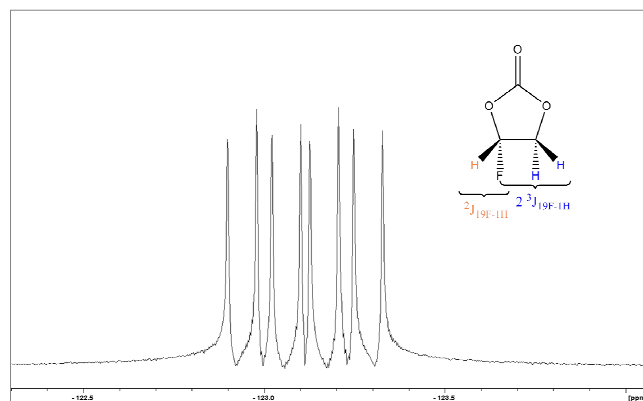


Figure 2: ¹⁹F-NMR spectrum of monofluoroethylene carbonate (ddd) with a chemical shift of -123.11 ppm and coupling constants as follows: ²J_{19F-1H} = 64 Hz, ³J_{19F-1H} = 33 Hz, ³J_{19F-1H} = 22 Hz.

Conclusion

Liquid NMR-spectroscopy, especially for heteronuclei, is a powerful method for electrolyte characterisation. Since the recording of NMR-spectra is useful for structure elucidation, it enables the monitoring of thermal degradation of different electrolytes (fig 1) or additives (fig 2) and the identification of

unknown electrolyte components, respectively. By using external standards and waiting long enough between two scans (extend d1) to be able to rely on the integrals of e.g. ¹⁹F-resonances, it's possible to determine whether one electrolyte system is more stable or not.

[1] K.Xu. *Chem. Rev.*, **2004**, 104, vol. 10

[2] S.F.Lux, I.T. Lucas, E. Pollak, S.Passerini, M. Winter, R. Kostecki, *Electrochem. Comm.*, **2012**, 14, 47-50

[3] J. S. Gnanaraj, E. Zinigrad, L.Asraf, H. E. Gottlieb, M. S. Precher, M. Schmidt, W. Geissler, D. Aurbach, *J. Electrochem. Soc.*, **2003**, 150, A1533-A1537