APPLICATION NOTE

Batteries:
The simplification of LiPF$_6$ hydrolysis by decoupling of $^{19}\text{F}$ and $^{31}\text{P}$
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Introduction

Over the last two decades, the use of lithium-ion batteries (LIBs) as an energy storage device has surged due to their uses in notebooks, cellular devices, and electric vehicles. As a result of their increasing popularity, interest in improving the performance of such batteries has proportionally increased. There are three primary components to LIBs that can affect their performance: the electrodes (anode and cathode), the separator, and the electrolyte (salt and solvent system). The electrolyte in the LIB plays a pivotal role as the medium enabling the movement of lithium ions between the anode and cathode. The electrolyte is often a complex mixture of aprotic solvents and lithium salt(s). To produce a successful electrolyte, factors such as salt dissociation, solubility, viscosity, ionic conductivity, chemical compatibility, and thermal stability need to be considered.$^{1,2}$

When it comes to electrolyte mixtures, it is crucial to ensure that all chemical species are of high purity. Introducing impurities into an electrolyte can interfere with the battery’s overall performance, which may ultimately lead to its failure. One of the most common lithium salts in electrolyte mixtures is lithium hexafluorophosphate (LiPF$_6$), partly due to it possessing an ideal combination of key characteristics (i.e., conductivity, dissociation constant, ionic mobility, and stability), superior to that of other lithium salts. However, LiPF$_6$ has limited thermal stability and is prone to hydrolytic decomposition, which not only leads to decreased battery performance, but also becomes a health hazard.$^3$ As a result, further understanding of the hydrolytic decomposition processes is needed. Unfortunately, there are a limited number of publications reporting on the decomposition of LiPF$_6$, and the literature shows that these hydrolysis processes are highly dependent on the solvent system used, making these studies more strenuous. The scheme below depicts the expected hydrolysis pathway of LiPF$_6$ in the presence of water. Note that the presence of other solvents in the electrolyte solution will influence the decomposition by-products and available reaction pathways.$^3$

Scheme 1. Expected decomposition pathway for LiPF$_6$ hydrolysis.$^3$

The hydrolysis of LiPF$_6$ can be conveniently monitored via nuclear magnetic resonance (NMR) spectroscopy. Although $^1$H remains the most popular and widely observed nuclide in NMR spectroscopy, $^{19}$F and $^{31}$P are better suited for this application due to their larger chemical shift ranges, the absence of protons in LiPF$_6$, and the reduced dynamic range between the impurities that are formed and the electrolytes in solution. While it might initially seem promising, $^7$Li NMR could not be used to monitor the decomposition of LiPF$_6$ since Li$^+$ ions in solution result in a single averaged signal, which cannot be used to directly observe decomposition.

Analysis

To monitor the hydrolysis of LiPF$_6$, 0.1 mL of HzO was added to 0.6 mL of a 1 M solution of LiPF$_6$ in a mixture of ethylene carbonate and dimethyl carbonate 50% (v/v). The reaction was followed using one-dimensional $^{19}$F, $^{19}$F($^{31}$P), $^{31}$P, and $^{31}$P($^{19}$F) benchtop NMR spectroscopy with the Nanalysis 60PRO instrument.

Figure 1. Left: Stacked plot of $^{31}$P (24.5 MHz) NMR spectra obtained over a period of 72 hours to monitor the hydrolysis of LiPF$_6$. Right: Stacked plot of $^{31}$P($^{19}$F) (24.5 MHz) NMR spectra obtained over a period of 72 hours to monitor the hydrolysis of LiPF$_6$. Time 0 is represented by the bottom spectrum and LiPF$_6$ is referenced at -145.0 ppm.

Figure 2. Left: Stacked plot of $^{19}$F (57.0 MHz) NMR spectra obtained over a period of 72 hours to monitor the hydrolysis of LiPF$_6$. Right: Stacked plot of $^{31}$P($^{19}$F) (57.0 MHz) NMR spectra obtained over a period of 72 hours to monitor the hydrolysis of LiPF$_6$. Time 0 is represented by the bottom spectrum and LiPF$_6$ is referenced at -74.5 ppm.

Figures 1 and 2 show the steady decrease of the LiPF$_6$ with a concomitant increase in impurities as decomposition proceeds. Using the Kinetics module on the Nanalysis 60PRO, the decomposition reaction was followed for 72 hours in total, with data acquisition every hour. Reaction rates can feasibly be determined for each chemical species in solution by integrating their respective signal regions; however, the presence of significant coupling between $^{19}$F and $^{31}$P complicates this process as additional decomposition by-products appear over time and overlap with existing integration regions. As shown in Figure 3, the hydrolysis of LiPF$_6$ yields multiple impurities when observing $^{19}$F and $^{31}$P NMR; the identification of these impurities is made more cumbersome due to coupling of heteronuclei (Figure 3A and 3C). Although these impurities have been identified in the literature, analogous systems, which differ by their respective salts or electrolytes, have not been studied to the same extent, and consequently, can give more ambiguous results that are difficult to interpret.$^{1,2}$ The ability to use $^{19}$F($^{31}$P) and $^{31}$P($^{19}$F) experiments
As demonstrated in this application note, the use of heteronuclear decoupled NMR is a very powerful way of analyzing the decomposition of LiPF$_6$. While regular one-dimensional heteronuclear NMR remains useful, the simplification of data by decoupling heteronuclei such as $^{19}$F and $^{31}$P can expedite the deconvolution and analysis of analogous salt systems. With increasing research being performed in energy storage, having a fast and efficient method at your disposal would be a significant asset. If you would like to know more about battery applications using NMR spectroscopy or are interested in how this technique could be incorporated into your workflows, please do not hesitate to contact us.

References