Application note | 000243

Industrial analysis

Robust and sensitive measurement of trace element impurities in $LiPF_6$ electrolyte solutions using ICP-OES

Authors

Sukanya Sengupta, Bhagyesh Surekar, and Daniel Kutscher

Thermo Fisher Scientific, Bremen, Germany

Keywords

Battery production, ICP-OES, robustness, method validation, sensitivity, limits of quantification, analytical testing

Goal

To demonstrate the capabilities of the Thermo Scientific™ iCAP™ PRO XP ICP-OES Duo for sensitive, robust, fast, and straightforward analysis of trace elements in lithium hexafluorophosphate electrolyte samples

Introduction

Lithium ion (Li-ion) batteries are increasingly being used in electronic devices and electric vehicles (EV). The demand for electric vehicles is expected to grow significantly in the next years, as they can be a viable alternative to fossil fuel driven vehicles and help to rapidly decrease CO_2 emission from traffic. These developments have led to a growing industry demand for Li-ion batteries globally that is complemented by significant efforts in research and development, dedicated to providing efficient and cost-effective solutions[1]. For production, especially in the ramp-up phase, regular and rigorous quality control of all components, including the lithium salt, anode and cathode material, and electrolyte, of an Li-ion battery is crucial. The electrolyte plays an important role in the charging and discharging performance of the battery, and hence needs to be checked for potential impurities. At the same time, the electrolyte is also a sample type that allows the investigation of ageing processes, as degradation products from all components of the battery can accumulate within it over time. Finally, once the battery is at the end of its life, all components must be thoroughly screened to ensure that potential environmental contamination and injury risks to personnel disassembling the batteries are minimized.

One of the most common electrolytes in Li-ion batteries is lithium hexafluorophosphate ($LiPF_6$) dissolved in a binary or ternary mixture of ethylene carbonate (EC) and linear carbonates, such as diethyl carbonate (DEC) and ethyl-methyl carbonate (EMC). It is a popular electrolyte material in the industry due to its high energy density and power properties.[2,3] At the moment, there is only one standard method available for the analysis of electrolytes for lithium-ion batteries, based on the Chinese Standard HGT/ 4067-2015,[4] which requires method detection limits of 1 $mg{\cdot}L^{-1}$ in the final $LiPF_6$ electrolyte samples. The Thermo Scientific™ iCAP™ PRO ICP-OES Series can be the instrument of choice for this analysis, delivering detection limit performance well within the required range and providing a robust setup that can accurately characterize $LiPF_6$ electrolyte sample materials.

Experimental

Instrument parameters and experimental conditions

An iCAP PRO XP ICP OES Duo instrument was used in this study to carry out measurements of 15 trace elements that may be present as impurities in electrolyte samples. The instrument was operated using intelligent full range (or iFR) mode, allowing a complete screening of the UV as well as the visible part of the spectrum in one single exposure. Due to the sensitivity requirement, the plasma was observed axially.

The nature of the samples, a unique combination of organic solvents with traces of HF formed due to the partial hydrolysis of the PF_6^- anion, demands careful selection of a compatible sample introduction system. Every component must be fully compatible with the chemistry of the sample and the matrix, so an inert nebulizer and spray chamber, as well as a ceramic torch and an alumina-based injector, were used. Details of the sample introduction setup and instrument parameters are listed in Table 1. Use of personal protective equipment, including gloves, laboratory glasses, and coat, while handling the samples is essential. A suitable cover for the autosampler containing the samples is also required.

$LiPF_6$ in organic solvents can be challenging to handle and analyze, particularly over longer measurement sessions spanning several hours. The high carbon content, coming both from the diluent and the organic carbonates present in the matrix, along with the presence of HF, leads to analytical challenges including high background signals, injector blockage, and high plasma load, leading to instability or even extinguishing of the plasma. The optimized experimental parameters developed in this method, together with the inherent robustness of the iCAP PRO Series ICP-OES overcome these challenges and ensure stable, sensitive, and accurate analysis with low sample measurement times. The iCAP PRO XP ICP-OES Duo brings advantages like full flexibility for method development and the option to use the extended UV (or eUV) mode for even more sensitive observation in the UV range, making it an ideal choice of instrument for this method.

Table 1. Instrument configuration and typical operating parameters

Instrument parameter	Setting
Spray chamber	PTFE HF resistant spray chamber
Nebulizer	Burgener PEEK MiraMist™
Center tube	1.0 mm alumina injector
Torch	Demountable ceramic D-Torch
Pump speed	30 rpm
Pump tubes	Phthalate-free Solva orange/white Phthalate-free Solva white/white
Uptake time	70 s
Wash time	70 s
Nebulizer gas flow	0.30 $L{\cdot}min^{-1}$
Auxiliary gas flow	0.5 $L{\cdot}min^{-1}$
Coolant gas flow	15 $L{\cdot}min^{-1}$
RF power	1,250 W
Repeats	3
Exposure time	10 s Axial iFR

Sample preparation

Three different electrolyte samples were measured in this exercise. These were fresh unused $LiPF_6$ electrolyte solutions in organic solvent mixtures like EC + EMC and EC + DEC. Approximately 2.5 g (~2 mL) of electrolyte samples were accurately diluted in 50 mL of an organic diluent consisting of 5% (v/v) EMC and 20% (v/v) ethanol in 18 MΩ·cm ultra-pure water.

Standards and reference materials

A calibration blank and a set of calibration and linearity standards containing the 15 target elements up to 1,000 $\mu g{\cdot}L^{-1}$ concentration (0, 50, 200, 500, and 1,000 $\mu g{\cdot}L^{-1}$) were prepared in the same diluent as the samples using single element standards (1,000 $mg{\cdot}L^{-1}$, SPEX™ CertiPrep Group, Metuchen, US) of individual analytes. 5 $mg{\cdot}L^{-1}$ yttrium was added as an internal standard to all samples and calibration solutions in order to track and compensate for matrix effects.

Quality control and method validation

The 200 µg·L^{-1} calibration solution was used as a quality control (QC) standard to ensure that good analytical precision was achieved throughout the analysis. To ensure method validity, selected samples were spiked with 50 µg·L^{-1} of the target elements and analyzed by the same method used for all other analyses in this study (Table 1). Spiked samples were also included in a robustness test to estimate analytical accuracy and precision over a long session of measurements.

Data acquisition and data processing

The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software was used for data acquisition, processing, and reporting. Qtegra ISDS Software contains a full feature set for quality control tests performed during the analysis.

Results and discussion

Selectivity, sensitivity, and linearity

Wavelengths with the highest sensitivities in the high carbon matrix of the samples were selected for the analysis. Qtegra ISDS Software provided the flexible option to select background and peak positions freely and even remove background positions from one side or the other of a peak in case of any interference, which ensured accurate calculation of the concentrations of all elements in the solutions being analyzed.

The limit of detection/instrument detection limit (LOD/IDL) and method detection limit (MDL) were calculated based on repeat measurements of blank and low concentration calibration standards and the dilution factor used for sample preparation. The LODs and MDLs for each element are listed in Table 2.

The calibration linearity of the developed method was tested up to concentration levels of 1,000 µg·L^{-1} for all elements. The calibration curves for the different wavelengths gave R^2 values of between 0.9991 and >0.9999 over the entire calibration range (some examples of calibration curves are shown in Figure 1).

Table 2. List of suitable wavelengths, lowest limits of detections (LOD), R^2 values, and method detection limits (MDL) for individual elements

Element	Wavelength (nm)	Mode	LOD (µg·L^{-1})	R^2	MDL (mg·L^{-1})
Al	167.079	Axial-iFR	0.50	0.9998	0.010
As	193.759	Axial-iFR	7.57	0.9998	0.151
Ca	393.366	Axial-iFR	3.52	0.9991	0.070
Cd	214.438	Axial-iFR	0.18	0.9999	0.004
Co	238.892	Axial-iFR	0.34	0.9998	0.007
Cr	283.563	Axial-iFR	0.06	0.9997	0.001
Cu	324.754	Axial-iFR	0.60	0.9994	0.012
Fe	238.204	Axial-iFR	0.46	0.9999	0.009
Hg	253.652	Axial-iFR	6.28	0.9999	0.126
K	766.490	Axial-iFR	1.28	0.9998	0.026
Mg	279.553	Axial-iFR	0.05	0.9997	0.001
Na	589.592	Axial-iFR	3.88	0.9991	0.078
Ni	231.604	Axial-iFR	0.70	0.9998	0.014
Pb	220.353	Axial-iFR	4.92	0.9999	0.098
Zn	213.856	Axial-iFR	1.56	0.9997	0.031

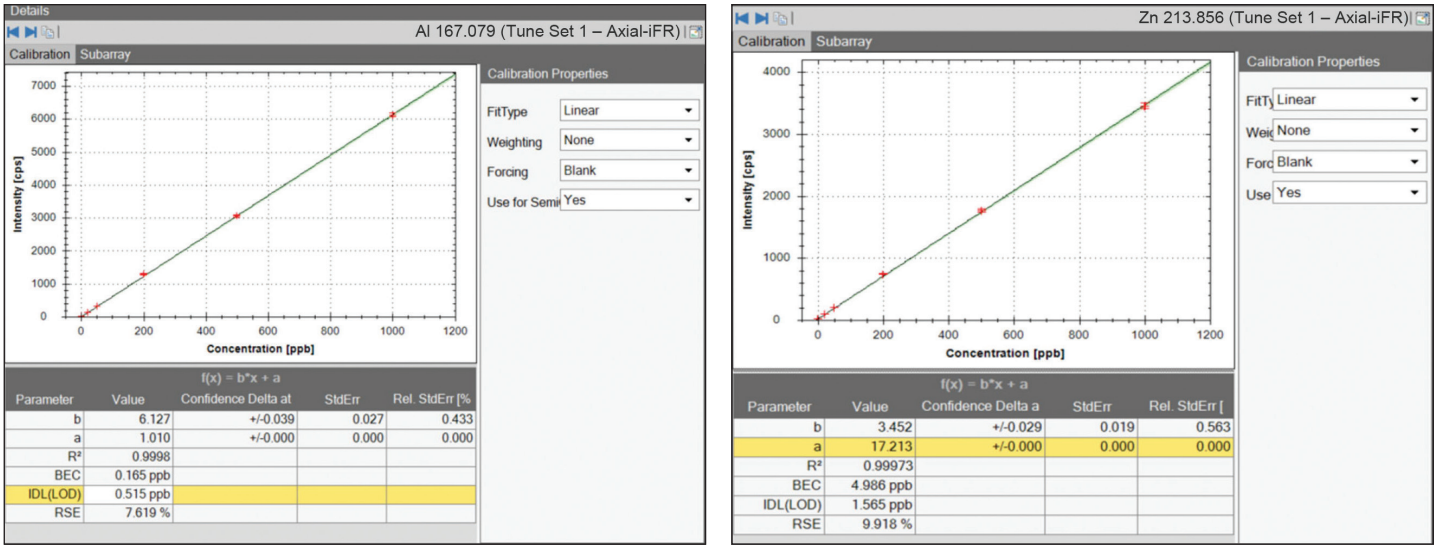

Figure 1. Examples of calibration curves obtained using the developed method

Accuracy

The accuracy and precision of the method was assessed by monitoring the concentration recoveries of two fresh electrolyte samples spiked with 50 µg·L^{-1} of the target elements. Recoveries were found to be within the accepted range of 80 to 120%, with most elements showing >90% (Table 3). A recovery of the internal standard (5 mg·L^{-1} yttrium) of around 90% in fresh electrolyte sample matrices demonstrated low matrix suppression, further ensuring data accuracy.

Robustness validation over a typical working day

The developed method was tested for its robustness, i.e., its ability to deliver accurate and precise results when longer sequences are run in a laboratory, as may occur in a production facility environment. The samples described above (native and spiked solutions of the two fresh electrolytes) were set up as an uninterrupted measurement over several hours, repeated on different days. The objective of this test was to prove that the sample matrix (containing significant amounts of ethanol as part of the diluent) can be run without the occurrence of signal drift or interruptions due to failure of applicable QC checks or limits set for the recovery of the internal standard. The sequence started with the calibration block, including blanks and standards, followed by an initial QC check (ICV = Initial Calibration Verification). The QC sample was regularly analyzed after every 20 unknown samples. A spiked sample was also measured occasionally throughout the robustness test.

The internal standard recovery, QC sample concentration recovery, and spiked concentration recoveries all remained stable throughout the experiment. Internal standard recovery was consistently between 85 and 90% for a measurement sequence of longer than 6 hours, as shown in Figure 2. The slightly lower recovery of the internal standard in real samples (compared to the calibration solutions) is due to the additional matrix contribution from the electrolyte samples (organic carbonates and elevated lithium content). However, despite the slight suppression the application of the internal standard allowed these matrix effects to be fully overcome (as demonstrated by the accuracy of the spike recovery test), and, more importantly, the sample matrix could be analyzed for an extended period of time (greater than 6 hours) without drift of the analytical system occurring. The QC recoveries were also found to be within a narrow range of 80–100% for all analytes, with the exception of sodium, which showed a slightly lower recovery of 76–78% for some samples in the test. The results of all QC checks analyzed as part of the study are shown in Figure 3. The recovery of the 100 µg·L^{-1} spike in the spiked electrolyte samples demonstrated very good accuracy (86–103%) and stability (RSD 1.5–4.7%) throughout the robustness test (Figure 4).

The trace elemental compositions of the electrolyte samples, corrected for the sample dilution, are presented in Table 4

Table 3. Spike recoveries on fresh electrolyte samples. Concentrations are in sample solutions that were measured directly, with no dilution factors applied.

			Concentrations (µg·L^{-1})			Concentrations (µg·L^{-1})		
Element	Wavelength (nm)	Mode	Sample 1 measured value	50 µg·L^{-1} spiked Sample 1	Spike recovery %	Sample 2 measured value	50 µg·L^{-1} spiked Sample 2	Spike recovery %
Al	167.079	Axial-iFR	<DL	50.6	97.7	<DL	48.5	93.9
As	193.759	Axial-iFR	<DL	50.2	115.6	<DL	52.4	94.1
Ca	393.366	Axial-iFR	15.8	59.7	87.8	<DL	57.9	112.3
Cd	214.438	Axial-iFR	<DL	48.2	96.7	<DL	45.6	91.3
Co	238.892	Axial-iFR	<DL	49.0	98.0	0.1	46.6	93.1
Cr	283.563	Axial-iFR	0.6	50.2	99.3	0.8	48.2	94.7
Cu	324.754	Axial-iFR	<DL	53.9	108.0	<DL	52.7	106.6
Fe	238.204	Axial-iFR	2.2	48.6	92.8	3.8	49.6	91.6
Hg	253.652	Axial-iFR	<DL	40.7	83.5	<DL	40.2	80.1
K	766.490	Axial-iFR	29.3	73.6	88.5	12.9	N.A.	N.A.
Mg	279.553	Axial-iFR	4.4	54.2	99.5	2.5	52.0	98.9
Na	589.592	Axial-iFR	29.3	73.6	88.5	11.2	69.7	117.0
Ni	231.604	Axial-iFR	2.7	45.9	86.4	<DL	42.1	86.6
Pb	220.353	Axial-iFR	<DL	50.5	107.1	1.3	50.4	98.2
Zn	213.856	Axial-iFR	10.9	59.3	96.9	2.5	56.7	108.3

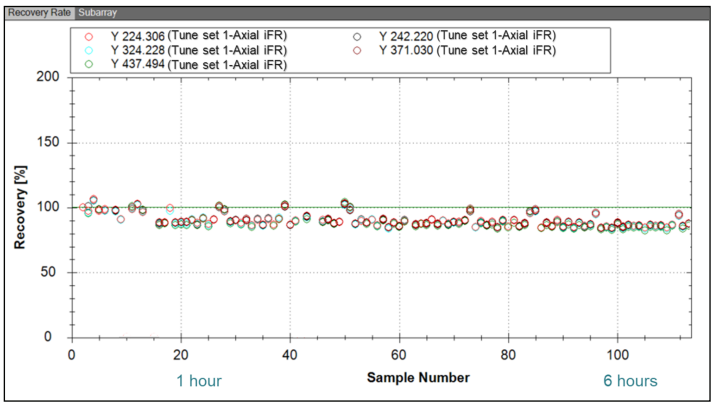

Figure 2. Internal standard recovery in samples and standards during an extended measurement sequence covering more than 6 hours

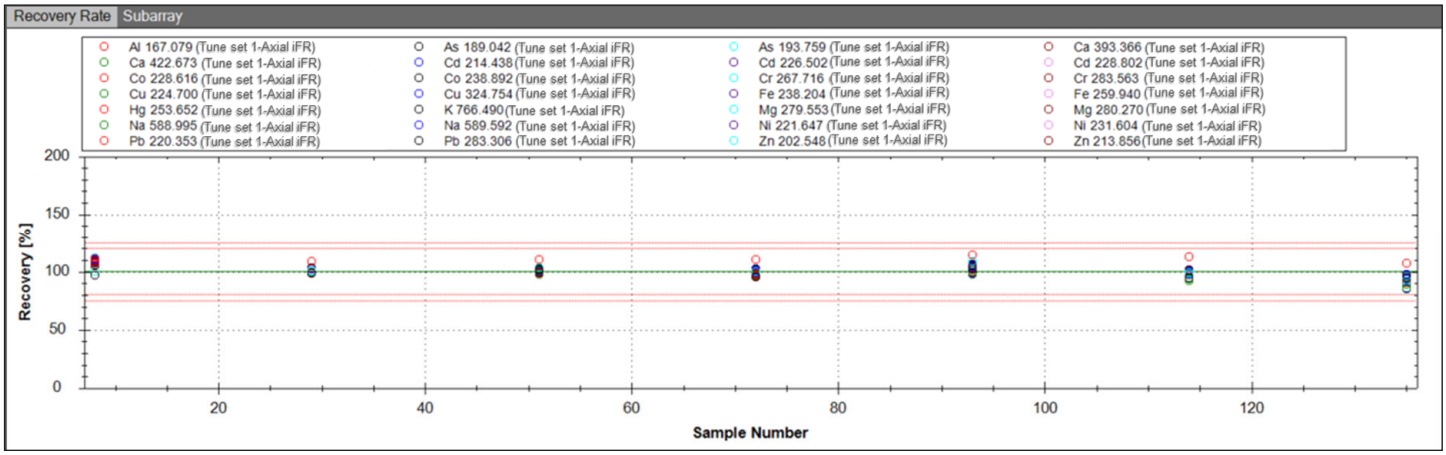

Figure 3. Robustness data demonstrating CCV (continuous calibration verification) recoveries of target elements in a QC standard (200 µg·L^{-1}) during a 7-hour experiment. The red lines mark the acceptable QC recoveries of between 80 and 120%. This figure is a direct export from the software for quick and easy data visualization.

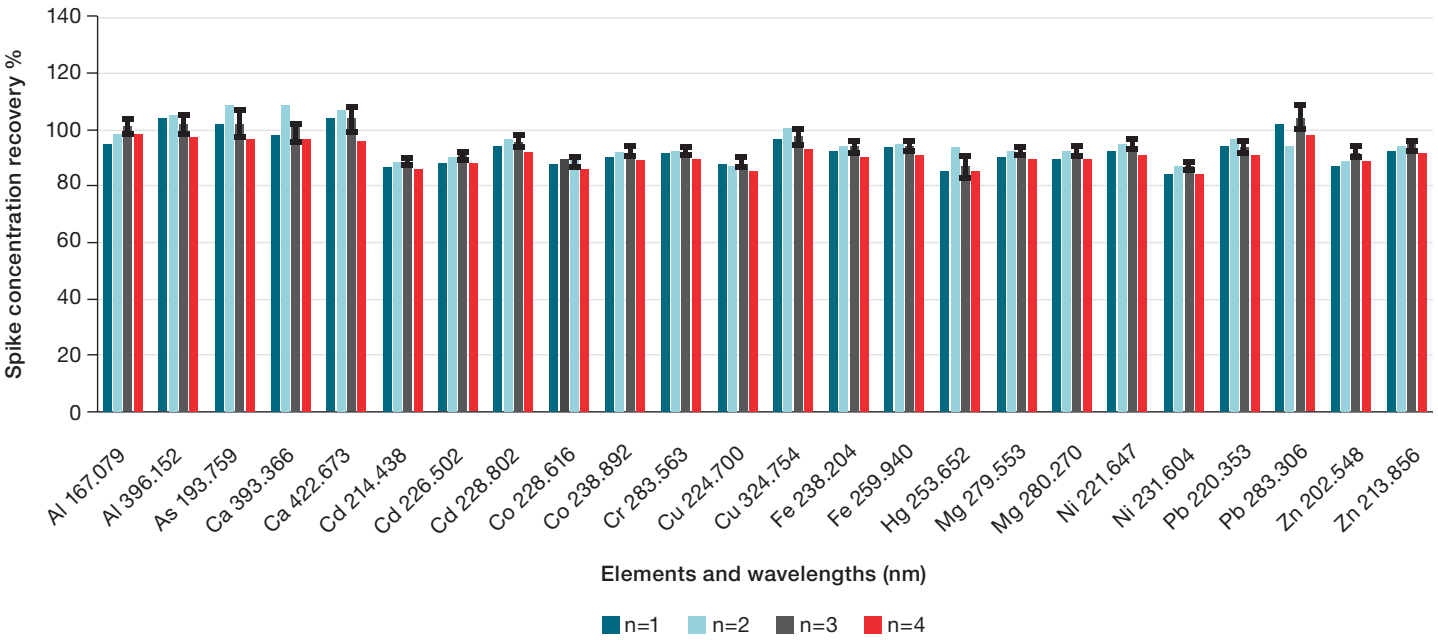

Figure 4. Concentration recoveries of a spiked electrolyte sample during the robustness test. The spiked sample was run on 4 occasions throughout a 7-hour sequence.

Table 4. Trace elemental composition of the fresh electrolyte samples (dilution corrected). Only elements detected in the quantifiable range have been reported here.

Element	Sample 1		Sample 2		Sample 3	
	Concentration (µg·L^{-1})	SD (1σ)	Concentration (µg·L^{-1})	SD (1σ)	Concentration (µg·L^{-1})	SD (1σ)
Al	<DL	-	<DL	-	<DL	-
Ca	316	13.1	<DL	-	<DL	-
Cr	12	2	16	0.15	10.0	1.9
Fe	44	0.5	76	0.12	100	3.1
K	<DL	-	260	0.35	321	8.7
Mg	12	2.7	50	0.004	6.6	3
Na	666	5.7	227	0.21	273	10.1
Ni	54	-	<DL	-	<DL	-
Zn	218	8.0	<DL	-	<DL	-

Conclusions

This study has demonstrated the performance of the iCAP PRO XP ICP-OES Duo system for highly sensitive and accurate analysis of impurities in electrolyte solutions containing $LiPF_6$ and organic carbonates, such as ethyl carbonate and ethyl methyl carbonate. The proposed method allowed for fast sample turnaround times combined with high reproducibility and robustness, allowing reliable analysis of long sequences over multiple days of analysis.

A summary of the main results and conclusions is presented below:

- Excellent sensitivity, sufficient for detecting impurities in $LiPF_6$ electrolyte samples (in the low µg·L^{-1} (ppb) range), was achieved for all the target elements using the Axial iFR mode of the instrument. A large linear dynamic calibration range of up to 1,000 µg·L^{-1} was also obtained. The linear dynamic range could be further expanded, if required, by adding standard solutions with higher concentrations. This would be beneficial when analyzing, for example, used electrolyte samples for battery ageing studies or failure diagnostic purposes.
- The accuracy of the method was verified by successfully recovering known spiked concentrations in fresh electrolyte samples in spite of the challenges arising from the sample matrix composition.
- Excellent system robustness and reproducibility was demonstrated over multiple days, proving the reliability of the method, with accuracy over long measurement runs validated by analysis of QC solutions, spiked samples, and internal standards.
- Daily continuous measurements of more than 6 hours are possible with the described method. Using a short exposure time of 10 s ensured not only fast analysis (3 min 6 s/sample), but also high sensitivity. A total of more than 100 samples could be measured daily following this approach. This high sample turnaround with consumption of low sample volumes, minimal downtime, and no need for extensive sample preparation or user interaction positions the iCAP PRO XP ICP-OES Duo system as an effective choice of instrument for quality control and characterization of trace elements in fresh electrolyte samples.

References

1. Lithium Batteries — new materials, developments and perspectives; Pistoia, G., Ed.; Elsevier Science: Amsterdam, 1994.
2. Scrosati, B., Insertion Compounds for Lithium Rocking Chair Batteries. In *Electrochemistry of Novel Materials;* Lipkowski, J.; Ross, P.N., Eds.; VCH: New York, 1993, pp 111-140.
3. Wu, W.; Yang, X.; Zhang, G.; Chen, K.; Wang, S. Experimental investigation on the thermal performance of heat pipe-assisted phase change material based battery thermal management system. *Energy Convers. Manag.* **2017**; 138, 486–92.
4. Cell liquor of lithium hexafluorophosphate. **https://www.chinesestandard.net/PDF/English.aspx/HGT4067-2015**

Learn more at **thermofisher.com**