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Application News

Nexis GC-2030 combined with Polyarc reactor

Determination of Lithium-Ion Battery Electrolyte Composition with Polyarc Microreactor

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User Benefits

- High accuracy quantitative determination of electrolyte composition
- Result directly from one measurement without external and internal calibration

Introduction

The production of the electrolytes for lithium-ion batteries takes place at different places globally. For quality assurance it is essential to determine the precise composition of organic carbonates. Variations in their composition can significantly affect battery performance and safety. Accurate analysis ensures that manufacturers can maintain consistent quality and meet the stringent requirements of the industry, leading to more reliable and efficient energy storage solutions.

The producers typically provide the weight percentages (%w) as the given composition. To determine this composition different analytical technologies can be used, typically GC-FID, GC-MS, LC or NMR. All of these technologies (except for NMR) have one thing in common: they all provide molecule-dependent responses. In other words, to determine the weight percentages (%w), an external calibration with all expected compound standards would need to be performed.

This is a common practice and typically does not pose a problem in routine operations. Nevertheless, for semi-routine and non-routine laboratories this leads to a significant time investment. In this article, we present a new, highly accurate GC-based method without the need for external or internal calibrations.

The Polyarc system has a catalytic microreactor that enhances gas chromatographs with flame ionization detectors (FIDs) by converting all organic compounds to methane molecules prior to their detection by the FID, therefore converting the FID into a quantitative carbon detector (QCD). An additional advantage of this approach is that by eliminating complex calibrations, the accuracy of quantification is significantly enhanced.

Sample Preparation and Measurement

25 µL LIB electrolyte with 1M $LiPF_6$ has been diluted with 1 mL dichloromethane and centrifuged for 5 min at 8500 rpm. The centrifuged solution was transferred into a 2 mL GC glass vial and measured by GC–2030 with Polyarc reactor.

The Package

For this application, a Shimadzu GC-2030 with liquid sampler AOC-30i (Figure 1, left) and Polyarc reactor (Figure 1, right part) was used.

Figure 1 Shimadzu GC-2030 with AOC-30i (left) and Polyarc reactor (right)

The recommended analytical hardware and software configuration is listed below.

- *Main Unit*

Nexis GC-2030 gas chromatograph with FID-2030 detector and Polyarc catalytic microreactor

- *Accessory*

AOC-30i liquid sampler

- *Main Consumables*

SH-5 column (30 m × 0.25 mm × 0.25 µm; P/N 221-75701-30)

- *Software*

LabSolutions LCGC

Results and Discussion

The obtained results of two different measured electrolytes are shown in Figure 2.

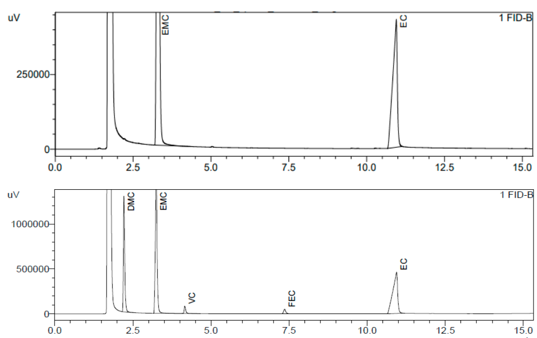

Figure 2 Obtained chromatograms of two measured LIB electrolytes. Sample 1 (top) and Sample 2 (bottom)

The two measured electrolytes are slightly different in composition of main carbonates and additives. Both represent quite typical products often used for LIBs manufacturing. For both a manufacturer's specification of the weight percentage (%w) is available. The original specifications may slightly differ from the really quantified values. The reason for that is the native decomposition and rearrangement of carbonates already during the storage. As long as the decomposition occurs only on a small scale, it does not have any impact on the quality of the electrolytes.

Since the Polyarc reactor converts all substances to methane before the FID, providing a molecule-independent response, the calculation of weight percentages (%w) using this approach is very straightforward. Basically, the software integrates the related compounds (main compounds and additives) peak areas and calculates the % of areas out of these values. The obtained % of areas are at the same time the needed %w of all integrated compounds.

This technology even does not require an accurate and precise sample preparation, the sample amount should just not overload the reactor and FID. Not presented within this application note, but a possible feature is the calculation of decomposition/purity grade. In that case the sum of peak areas of the target components are compared to the sum of peak areas of the unknown components in a percentage relationship. These two % areas are then the %w between the targeted compounds and destruction decomposition products (or impurities) in the electrolyte.

The calculated %w of the investigated electrolytes in comparison to the manufacturer specifications are shown in Table 1. The electrolytes were measured three times to calculate the %RSD.

Table 1 Obtained results for %w calculations

Compound		DMC	EMC	DEC	VC	FEC	EC
Sample 1	Peak area average	n.d	11969890	n.d	n.d	n.d	4430757
	%RSD	---	0.2	---	---	---	0.5
	Calculated %w	---	73%	---	---	---	27%
	Specified %w	0	70%	0	0	0	30%
Sample 2	Peak area average	3894856	6076716	n.d	294409	263520	4918256
	%RSD	0.8	0.6	---	0.8	0.5	0.7
	Calculated %w	25.2%	39.3%	---	1.8%	1.7%	32%
	Specified %w	27-29%	35-37%	0	1.7-2.5%	1.7-2.5%	34-38%

The results shown in Table 1 demonstrate a very high accuracy in the RSD of weight percentage calculations, with all components being <1%. The correlation between the calculated weight percentages and those provided by the manufacturers also shows a very good agreement. Minor differences arise, as mentioned earlier, due to prior storage, transportation, and sample preparation. Overall, Table 1 clearly indicates that a reliable correlation between the measured values and the specifications is possible, thus ensuring a dependable quality assurance analysis.

■ Conclusion

This application demonstrated the suitability of the Shimadzu GC-2030 with Polyarc reactor to fulfil a common request for the quality assurance of LIB electrolytes. Within only one measurement and without any additional time it is possible to obtain high accuracy results. Polyarc reactor is an important add-in to a classical GCMS analysis in this field, where the MS is used for confirmation and identification and the Polyarc-FID as a detector for the reliable quantification of sample composition.

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