

Full Survey Chemical Analysis of Materials Used in Lithium Ion Batteries

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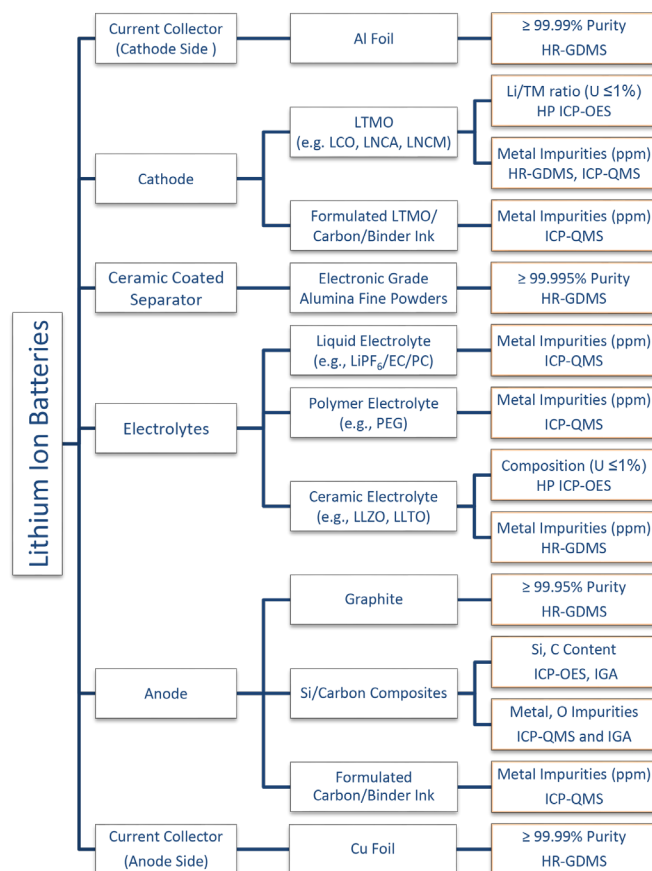
INTRODUCTION

In lithium-ion batteries (LIB), energy storage and release are provided by the movement of lithium ions between the cathode and the anode via a suitable medium that is called the electrolyte. In LIB systems, the anode (positively charged) electrode serves as the lithium source and the anode (negatively charged) electrode as the host for lithium ions. Currently manufactured LIBs are based on variety of chemistries that were developed and selected from wide-ranging variation of suitable materials and electrochemical systems that had been tailored and optimized for specific performance requirements, lifetime needs and, of course, safety (Scheme 1).

It is beyond doubt that LIBs have tremendous potentials for supporting large-scale energy storage technologies. However, manufacturing cost is still a significant barrier to widespread implementation of LIBs especially into diversifications of energy sources for transportation markets. Most of the cost reduction thus far has been achieved by energy density increases. Further cost reductions can be expected through optimization of manufacturing processes. Manufacturing uncertainties arise mainly from fluctuation of processing parameters¹, but also from the quality of precursors and formulated intermediate products. Defects introduced by unwanted or unintentional impurities and composition off-stoichiometry, inevitable as the consequence of thermodynamics, are important sources of uncertainties. Like all dynamic systems, the interplay between structure defects and cell performance is strongly coupled. Off-stoichiometry-related crystal defects can destabilize the layered structure of cathode, for instance, thus shortening the cycle life, while impurity defects are known to participate in multiple chemical, physical and electrochemical processes that either accelerate aging or directly lead to failure of batteries:²

- Cell shorting due to internal electrical pathways triggered by metallic impurities
- Self-discharging from internal micro-batteries created by magnetic impurities
- Cell explosion triggered by outgassing from impurity catalyzed hydrogen formation and liquid electrolyte decomposition

Scheme 1 illustrates some of the chemical analysis techniques and methods that can help to evaluate the full compositions of materials that are currently used for manufacturing LIBs. For each component, we will discuss the sample characteristics,



Scheme 1: Chemical analysis techniques and methods suitable for sensitive elemental analyses and evaluation of full compositions of precursors and/or intermediate products used in LIB manufacturing.

HR-GDMS: high resolution - glow discharge mass spectroscopy; HP ICP-OES: inductively coupled plasma – optical emission spectroscopy, high performance mode; ICP-QMS: inductively coupled plasma – quadruple mass spectroscopy; IGA: instrumental gas analysis; LTMO: lithium transition metal oxide; LLZO: lithium lanthanum zirconium oxide; LLTO: lithium lanthanum tantalum oxide; U: expanded uncertainty with coverage factor k = 2 at ~95% confidence level.

specification requirement, and analytical challenges individually. Accordingly, the choice of the technique and the corresponding analytical characteristics including sampling size, elemental coverage, precision, accuracy, and limits of detection is going to be discussed.

I. Current collectors

High purity Al foil and Cu foil are generally used as current collectors for electrodes in a LIB assembly. HR-GDMS can be used to quantitatively measure the µg/g – ng/g (i.e., ppmw - ppbw) level impurities in these foils, including those catalyzing the corrosion

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of the foil and those compromising the long-term imperviousness to air and liquid. Purity certification and trace impurity analysis of electronic grade Al and Cu using HR-GDMS are well established by ASTM F1593 and F2405 methods.

II. LTMO cathode precursors and formulated intermediate products

Li/TM ratio determination of LTMO: one of the key specifications for LTMO feedstock is to have a small excess amount of Li above the stoichiometry. This excess of Li leads to the formation of a few percentages of spinel phase, which stabilizes the layered rock salt structure of LiCoO_2 phase to improve cycle performance. Recent advance in cathode material design is focused on cation-disordered, Li-rich LTMO, based on percolation theory. NIST High Performance ICP-OES test method is suitable to determine Li deficiency or excess in LTMO, with extended measurement uncertainty of $U < 1\%$ at approximately 95% confidence level, as compared to $U \sim 3\text{-}5\%$ of the traditional ICP-OES methods, by minimizing the instrument drift errors under normal analysis conditions.³

Impurity analysis of LTMO: elemental impurities can be directly analyzed by HR-GDMS or ICP-QMS after proper sample digestion and dilution. HR-GDMS can provide quantitative determination of impurities at sub-ppm detection limits, including halogen elements. ICP-QMS analysis is fully quantitative, with elevated detection limits due to high dilution required. Trace C and S is usually analyzed by Combustion – Infrared technique, with detection limits down to a few $\mu\text{g/g}$.

Impurity analysis of formulated cathode intermediate products: the cathode intermediate products are typically formulated with the composition of 97-98 wt% LTMO, 1-2 wt% PVDF binder and conductive carbon. Magnetic impurities (such as Mg, Cr, Fe, Cu, Zn, Zr) introduced by the formulation process ideally should be controlled to sub- $\mu\text{g/g}$ level. Solution based ICP-QMS is the preferred technique for representative, high sensitivity quantification of these impurities. Because of the chemical resistance of PVDF binder and conductive carbon to most digestion media, high power microwave digestion using acid mixture with strong oxidizing power would be essential to ensure the proper recovery of these analytes. In general, detection limit of 0.1 $\mu\text{g/g}$ can be achieved for the magnetic impurities listed above.

III. Graphite and Si/C composite anode precursors

Impurity analysis of graphite: graphite suitable for battery application requires a purity greater than 99.95%. Overall impurity level of graphite can be assessed by ash content per ASTM C561 testing method. For high purity graphite used for anode precursors, at least half kilogram of sample needs to be ashed in order to generate sufficient amount of ash for statistically meaningful measurements. ASTM D8168 established ETV-ICP-OES as the technique for impurity analysis of graphite materials. The technique has been used for developing a graphite certified

reference material BAM CRM S009. The technique typically samples a few mg each analysis. On the other hand, HR-GDMS has been well established as an industrial production support tool to certify 5N+ purity, fully graphitized carbon materials used as anode precursors. HR-GDMS analysis samples similar or slightly larger amount of materials than ETV-ICP-OES. The typical reporting limits by HR-GDMS is listed in the Appendix.

Composition analysis of Si/C composites: Si-doped carbon composites have begun to enter industrial scale production as replacement to traditional graphite anode precursors with higher Li storage capacity. The specification calls for controlling both Si and C content. Due to the inherent two-phase structure, solution-based technique such as ICP-OES is recommended for accurate determination of Si content, and combustion – IR technique for carbon determination. At Eurofins EAG laboratory, we have developed analytical protocols that can achieve measurement precision of RSD $< 1\%$ for both elements.

Impurity analysis of Si/C composites: the inherent heterogeneous structure obsoletes most direct solid sampling techniques for quantitative impurity analysis. In this regard, ICP-QMS is the recommended technique. In Eurofins EAG laboratory, we modified the SEMI PV-49 method to establish the precision and accuracy for metal impurities in Si/C composites. Aside from metal impurities, oxygen is another key impurity, since formation of Si-O and C-O moieties will reduce the Li storage capacity. Inert Gas Fusion – Infrared is the recommended technique to evaluate bulk oxygen content down to $\mu\text{g/g}$ level. This technique is also capable of speciating oxygen bonding chemistry quantitatively with temperature ramping.

IV. High purity alumina fine powders for ceramic coating

Impurity analysis of alumina fine powder: ceramic fine powders used to coat separators are predominately alpha phase alumina with purity greater than 99.999%. Due to the challenge in digesting alpha-alumina, solution-based ICP-QMS is restricted only to analyze a few mobile ions such as Na, K, etc., whereas direct solid sampling HR-GDMS is used as a production control tool for monitoring majority of trace element impurities. The GDMS method is established using two alumina reference materials, CRM 8006A and CRM 8007A, with certified values for B, F, Na, Mg, Si, Cl, Ca, Ti, V, Cr, Mn, Fe, Cu, Zn, Ga, Sr, Zr, Ba, Nb, Mo, W, and Au. The typical reporting limits of HR-GDMS are listed in the Appendix.

V. Glass and ceramic solid electrolytes

Composition analysis of LLZO and analogs: Solid electrolytes hold potential as safer, longer-lasting and higher energy density alternatives to liquid electrolytes. Among solid ceramic electrolytes, lithium superionic conductors, such as $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), are highly promising. Various doping strategies have been developed to stabilize the highly Li-ion conductive cubic phase, including the Li site substitution with Al, Fe, Ge, and Ga, the La site substitution

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with Sr, Y and Ce, and the Zr site substitution with Nb, Ti, Ta, W, Mo, etc. Evaporation of Li during solid state reaction and sintering can shift the stoichiometry pairing to a particular crystal space group. In this regard, HP ICP-OES is the recommended technique for high-accuracy and high-precision composition determination, similar to other complex oxides.⁴

Impurity analysis of LLZO and analogs: LLZO is usually fabricated into thin ribbon (~1 µm thick). Therefore, aside from concerns on impurities directly related to electrochemical performance, those affecting the microstructure, or prone to segregate into grain boundaries, must also be properly checked and controlled. Like other high performance ceramics, trace analysis of LLZO and the analogs by solution based ICP-QMS technique is beset by digestion challenge, high detection limits due to dilution, and complex mass interferences from matrix elements and digestion acid mixture. This leaves the solid sampling technique such as XRF, LA-ICP-MS and HR-GDMS as preferred options. In this regard, HR-GDMS is particularly effective because of its full survey impurity analysis capability, sub-µg/g detection limits for majority of elements, and quantification not relying on strict matrix-matching reference materials, which are not easily available, if available at all.

In summary, advancement in lithium ion batteries requires a comprehensive approach, from breakthrough of fundamental principles, to materials design and synthesis, to industrial manufacturing. Each processing step introduces defects into

battery components in its own unique way and calls for innovative characterization solutions with speed, robustness, sensitivity, precision and accuracy. It is clear already today that adaptation of advanced analytical techniques is key for discovering and validating new avenues toward batteries with higher energy density, higher power density, better rate capacity and longer cycle life, and for unravelling the unanswered degradation mechanisms and those to come. In this regard, Eurofins EAG Lab can help!

FOOTNOTES

- 1 O. Schmid et al. "Modeling the Impact of Manufacturing Uncertainties on Lithium Ion Batteries", *J. Electrochem. Soc.*, 2020, 167, 060501;
- 2 S. Fedorov et al. "Ultrahigh-Temperature Continuous Reactors Based on Electrothermal Fluidized Bed Concept", *Journal of Fluids Engineering*, 2016, 138, 044502-10; John C. Nardi, US Patent 6,828,064, 2004; Kai-Pin Huan et al. "Magnetic impurity effects on self-discharge capacity, cycle performance, and rate capability of LiFePO4/C composites", *J Solid State Electrochem.*, 2017, 21,1767-1775.
- 3 L. Schoeck et al. "High Performance Inductively Coupled Plasma – Optical Emission Spectroscopy (HP ICP-OES) for Composition Analysis of Complex Oxides", EAG white paper, 2019.
- 4 A. J. Samson, et al. " A bird's-eye view of Li-stuffed garnet type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ceramic electrolytes for advanced all-solid-state Li batteries", *Energy Environ. Sci.*, 2019,12, 2957-2975.
- 5 a) S. Nowak and M. Winter, "Elemental analysis of lithium ion batteries", *J. Anal. At. Spectrom.*, 2017, 32, 1833; b) P. Verma, P. Maire and P. Novák, "A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries", *Electrochim. Acta*, 2010, 55, 6332-6341

APPENDIX

Table 1: Summary of measurement uncertainty for composition analysis by various techniques

Materials	LTMO	LLZO	Si/C Composites	Intermediate Products
Technique	HP ICP-OES	HP ICP-OES	Si: ICP/OES C: Combustion - R	Precursor: ICP-OES, TGA Binder/Conductor: TGA
Sampling size	500 mg	500 mg	250 mg	500 mg
U, % relative*	<1%	<1%	Si: 3-5% C: 1-2%	3-5%
*U – expanded measurement uncertainty at approximately 95% confidence level				

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Table 2: Typical reporting limits of HR-GDMS and ICP-QMS analysis of LIB precursors and intermediate products for key elemental impurities ^a							
Key Impurities	HR-GDMS, µg/g				ICP-QMS, µg/g		
	Graphite	Alumina	LTMO	LLZO	Si/C Composites	Intermediate Products	Liquid/Polymer Electrolytes
O	-	-	-	-	5 ^b	-	-
Na	0.05	0.1	0.01	0.1	0.1	0.5	0.1
Mg	0.05	0.1	0.05	0.05	0.1	0.5	0.1
Al	0.1	matrix	0.01	0.1	0.1	0.5	0.1
P	0.05	0.1	0.01	0.1	1	5	1
S	0.05	0.5	0.05	0.1	-	-	-
K	0.05	0.5	5	5	1	5	1
Ca	0.01	0.5	0.05	10	1	5	1
Ti	0.01	0.05	0.01	0.01	0.1	0.5	0.1
V	0.1	0.5	0.01	0.1	0.1	0.5	0.1
Cr	0.01	0.05	0.01	0.1	0.1	0.5	0.1
Fe	0.01	0.1	0.01	0.1	0.1	0.5	0.1
Ni	0.05	0.1	matrix	0.1	0.1	matrix	0.1
Cu	0.05	0.5	0.5	5	0.1	0.5	0.1
Zn	0.05	0.5	0.1	5	0.1	0.5	0.1
Zr	0.05	0.1	0.1	matrix	0.1	0.5	0.1
Nb	0.05	0.05 ^c	0.5 ^c	0.5 ^c	0.1	0.5	0.1
Mo	0.05	0.5 ^c	0.5 ^c	0.5 ^c	0.1	0.5	0.1

a lower reporting limits achievable upon request; b O determined by Inert Gas Fusion – IR; c on Indium binder in flat cell geometry; “-” quantitation not attainable by the technique