Brazilian Journal of Analytical Chemistry
2022, Volume 9, Issue 36, pp 150–154

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Tackling sample preparation for elemental analysis in the lithium-ion battery industry

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Over the last years, there has been a growing awareness to stop global warming and to keep our planet healthy. It is clear that we need changes in our way of life and in our technology. We need ideas to use energy in a better way. A clear step is the move from combustion engines to electric vehicles. Batteries are evolving and Li-ion battery is the chosen technology so far. Consequently, we must understand how to improve batteries performance, and the chemical analysis of their components is a necessary step.
Materials for anodes, cathodes and electrolytes should be fully characterized. Microwave-assisted digestion has become an essential ally for sample preparation of battery materials before measurements by inductively coupled plasma optical emission spectrometry. We are going to demonstrate how the use of microwave-assisted closed vessel digestions makes feasible the metal analysis of several components used in the Li-ion battery industry. Moreover, this approach led to shorter digestion cycles, using lower volumes of reagents and higher temperatures without compromising safety aspects. The implementation of Li-ion battery technology aims to a more sustainable world, so a green approach should be taken to address this new analytical challenge. The developed procedures are fully compatible with green technologies and incorporate green chemistry attributes to improve our environment.

Keywords: Li-ion battery, Microwave-assisted digestion

INTRODUCTION

Battery is an electrochemical device to store energy and all batteries are composed of two electrodes connected by an electrolyte. According to Armand and Tarascon[1] “when these electrodes are connected by means of an external device, electrons spontaneously flow from the more negative to the more positive potential. Ions are transported through the electrolyte, maintaining the charge balance, and electrical energy can be taped by the external circuit. In secondary, or rechargeable, batteries, a larger voltage applied in the opposite direction can cause the battery to recharge”. Nowadays, Li-ion batteries are the choice to power portable electronics and hybrid/full electric vehicles. Nitta et al. stated that “Li-ion batteries have an unmatchable combination of high energy and power density”. These authors also listed fundamental advantages of Li-ion batteries: Li has the lowest reduction potential of any element and, consequently, Li-based batteries have the highest possible cell potential.[2] They also highlighted that Li is the third lightest element and has one of the smallest ionic radii of any single charged ion. These factors are related to the high power density of Li-ion batteries.

Processes of charge or discharge of Li-ion battery are based on electrochemical processes involving Li ions between these electrodes. Li-ion battery is composed by two electrodes, anode and cathode, and a polyolefin-based separator soaked with an electrolyte.

The performance of anode and cathode materials affects Li-ion batteries energy density, safety, and lifespan. One important aspect about the performance and lifecycle of these materials is related to their

composition and formed decomposition products along their lifetime. It is important to know the chemical composition of all components of batteries to better understand aging effects and expand their lifecycle. Consequently, chemical analysis is a must for determining stoichiometries of the active materials, their changes along charge/discharge cycles and impurities. Nowadays, elemental analysis is frequently based on plasma methods. Inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) are used depending on the required sensitivity. However, despite instrumental alternatives for direct solid analysis, both instrumental methods generally involve analysis of solutions introduced by pneumatic nebulization. It means that solid samples, i.e., anode, cathode and separator materials of batteries, should be converted in representative solutions before instrumental analysis. The sample preparation step exerts a pronounced effect on the quality of analytical results and inorganic materials used as electrodes in Li-ion batteries are hardly decomposed. Mixed oxides and carbon-containing materials are resistant to chemical attack and special procedures should be developed for efficient conversion of these materials in representative solutions.

Nowak and Winter[3] emphasized that considering the huge volume of publications it is astonishing that the research field of elemental analysis of batteries is in a so-early stage. They also stated that: "… it is clear already today, that the continuous improvement and adaptation of advanced analysis methods will be the key for the accurate chemical analysis of batteries and its components, thus unraveling the unanswered degradation mechanisms and those to come.".

Microwave-assisted digestion methods are applicable and less aggressive reagents can be used at high temperatures in closed vessels. Adopting this technology, green digestion procedures can be developed for sample preparation and these are fully compatible with the advent of a greener technology for powering devices and vehicles.

MATERIALS AND METHODS

Microwave-assisted Acid Digestion

Sample acid digestion was performed with two types of system based on different microwave technologies.

The ETHOS UP is a flexible and high performing platform used for elemental analysis. Equipped with easyTEMP contactless sensor, it directly controls the temperature of all samples and solutions, providing accurate temperature feedback to ensure complete digestion in all vessels and high safety. ETHOS UP works with SK-15 rotor capable of high temperature (up to 300 °C) and pressure (up to 100 bar). The SK-15 also features Milestone's patented "vent-andreseal" technology for controlling the internal pressure of each vessel. This ensures complete, safe and reproducible digestions of even the most difficult samples.

The ultraWAVE, developed and patented by Milestone, with Single Reaction Chamber (SRC) technology utilizes high-performance stainless steel, allowing to reach higher pressures and temperatures (up to 199 bar and 300 °C respectively) and to use any type of acids. Disposable vessels eliminate the need to assemble, disassemble or clean between processing. Just as important, dissimilar samples can be processed simultaneously using any mixture of disposable glass, quartz or TFM vials, thus saving time and money. The ultraWAVE is simply the fastest, easiest and most efficient digestion system ever made.

Digestion methods for Spodumene sample

ETHOS UP					ultraWAVE				
Sample mass	100 mg				100 mg				
Final volume	50 mL				50 mL				
Reagents	3 mL of H_3PO_4, 3 mL of H_2SO_4 and 2 mL of HF (dil 1:3)				1.5 mL of H_3PO_4, 1.5 mL of H_2SO_4 and 2 mL of HF (dil 1:3)				
	Microwave heating program				**Microwave heating program**				
		Time	Temp	Power		Time	T1	T2	Power
	1	25 min	230°C	1800 W	1	15 min	280 °C	60 °C	1500 W
	2	30 min	230°C	1800 W	2	20 min	280 °C	60 °C	1500 W

Digestion methods for $LiFePO_4$ (LFP) sample

ETHOS UP					ultraWAVE				
Sample mass	500 mg				500 mg				
Final volume	50 mL				50 mL				
Reagents	2 mL of HNO_3 + 6 mL of HCl				1 mL of HNO_3 + 3 mL of HCl				
	Microwave heating program				**Microwave heating program**				
		Time	Temp	Power		Time	T1	T2	Power
	1	25 min	230°C	1800 W	1	15 min	250 °C	60 °C	1500 W
	2	15 min	230°C	1800 W	2	20 min	250 °C	60 °C	1500 W

Determination of Metals

The instrument used for metals and trace metals determination was an inductively-coupled plasma optical emission spectrometer (ICP OES), with axial view and equipped with automatic sampler. The instrument setup and the operating conditions are reported in Table 1.

Table 1. ICP OES operating parameters

Parameter	Setting
RF applied power (kW)	1.3
Plasma gas flow rate (L/min)	15
Auxiliary gas flow rate (L/min)	1.5
Nebulizer gas flow rate (L/min)	0.75
Replicate read time (s)	5
Stabilization delay (s)	30
Sample uptake delay (s)	30
Pump rate (rpm)	15
Rinse time (s)	15
Replicates	3
Emission lines (nm)	Indicated in each table of data

Spike recoveries and Internal standard Spike standard

Three replicates out of six were spiked with 1000 µL of periodic table mix 1 (solution h) and 2 (solution i) for ICP standards respectively, immediately after sample weighing and prior to reagent addition. These worked as recovery studies for elemental impurities. The concentration of the spiked elements in the final digested solution was 200 µg/L. Internal standard. 10 µg/mL of Yttrium standard (d) was added to calibration standards, blanks, digested solutions and, where appropriate, to their dilutions (e.g.: 500 µL of Y std added to 50 mL of digested solution). This was used as internal standard to correct matrix effects.

RESULTS AND DISCUSSION

Spodumene is a pyroxene mineral consisting of lithium aluminum inosilicate ($LiAlSi_2O_6$). It is the most widely exploited mineral source of lithium (theoretical lithium content = 3.73%). Other lithium-bearing pegmatite silicates include lepidolite and petalite. Although in the past industry transitioned to extracting lithium from brines, nowadays the exploding demand for lithium has made the exploration for and development of spodumene deposits a highly attractive endeavor.

ETHOS UP and UW led to efficient digestions and results using ICP OES did not present any statistical difference. Consequently, we have decided not to specify for each set of results the used system because both led to accurate data.

Table 2. Major elements in Spodumene sample

	Determined concentration (%)	RSD% (n = 6)
Al 396.152	12.9	1.67
Li 670.783	2.95	0.92
Si 251.611	27.9	1.12

Lithium iron phosphate, $LiFePO_4$ (LFP), is extensively used in the lithium-ion battery field as cathode material. The main advantages of LFP are its flat voltage profile, low material cost, abundant material supply and better environmental compatibility compared to other cathode materials. In fact, LFP contains neither nickel nor cobalt, both of which are supply-constrained and expensive. The use of phosphates avoids cobalt's cost and environmental concerns. The purposes of LFP analysis are 1) to determine the composition of the main elements (QC/Production) and 2) to evaluate the purity of the raw material (QC/R&D).

Table 3. Major elements in $LiFePO_4$ (LFP) sample

	Determined concentration (%)	RSD% (n = 6)
Li 670.783	4.81	1.38
Fe 238.204	33.9	1.65
P 213.618	20.2	4.01
Ca 396.847	0.47	4.55
K 766.491	0.00844	3.54
Mg 279.553	0.000829	5.80
Na 589.592	0.00557	4.32

Table 4. Impurities and spike recoveries in $LiFePO_4$ (LFP) sample

	Determined concentration (µg/L)	RSD% (n = 3)	Spiked determined concentration (µg/L)	RSD% (n=3)	Spike recovery (%)
Ag 328.068	26.5	21.3	120	7.94	93
Al 237.312	16.6	2.45	121	1.34	105
As 193.696	72.1	10.4	179	1.79	106
Ba 455.403	<MDL		95.8	1.81	96
Be 313.107	<MDL		93.3	3.67	93
Cd 214.439	45.7	11.4	144	2.48	98
Co 238.892	<MDL		94.4	0.86	94
Cr 206.158	38.5	16.2	144	1.78	105
Cu 324.754	<MDL		95.0	0.56	95
Mo 202.032	<MDL		98.4	1.61	98
Ni 231.604	<MDL		91.9	0.68	92
Nb 313.078	<MDL		94.4	1.71	94
Pb 182.143	<MDL		97.3	0.84	97
Ru 240.272	76.9	7.4	169	3.70	93
Sb 206.834	<MDL		93.8	1.30	94
Sr 407.771	<MDL		95.6	3.35	96
Ti 336.122	<MDL		93.1	2.77	93
V 292.401	92.4	2.83	210	4.15	118
Zn 206.200	263	8.35	359	4.63	97

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