Sample Preparation and Analysis of Materials in Lithium-Ion Battery Production Using Sequential Microwave Digestion

Abstract

Currently there is a drive for research, development and implementation of the next generation of Lithium-ion (Li-ion) battery high-purity raw materials for improved performance of the basic battery components. Research initiatives are focused on the elemental composition, specifically aimed at replacing cobalt (Co) with the more abundant and easier to extract manganese (Mn). Meanwhile, testing the basic battery components including cathode, anode, separator, and even the electrolyte materials for elements down to the ppb level to improve battery performance is now the norm. The automated BLADE™ sequential microwave digestion system can safely operate at temperatures and pressures required to provide a more rapid and efficient acid extraction (leach) or total digestion of these materials, thus providing a more accurate analysis via inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). Different sample types, including various lithium sources, cathode materials, and anode material, were digested or leached, and analyzed. Samples were prepared and analyzed in triplicate. Standard reference materials (SRMs) and spiked samples were used to validate both the microwave method as well as the analysis. The BLADE was able to use both HF and non-HF acid mixtures to perform the digestions.

Introduction

Li-ion batteries are one in the long line of energy sources humans have used for transport machinery. Sources such as coal, biomass, and oil have been the predominant materials used in fueling transport, starting from the 18th century. With constant pushes towards greener energy sources and lower carbon emissions in the United States and internationally, many auto manufacturers are beginning to put more time and research into electric and hybrid vehicles using Li-ion batteries. Electric and hybrid cars are a worldwide phenomenon with more that 40 million electric vehicles sold since 2012. The demand for these vehicles as well as other consumer electronics such as laptops, cell phones, tablets, and power tools has never been higher. As the demand for electronic goods and greener vehicles goes up, production and scale for Li-ion batteries must also increase.

In addition to lithium, many other minerals such as iron (Fe), cobalt (Co), nickel (Ni), and manganese (Mn) are facing higher demand for ever changing anode and cathode formulations. The challenge is not only to be able to mine these elements to meet demand, but also refining these sources to provide the highest purity materials possible. Constant research and development on different anode and cathode materials also requires full knowledge of the elemental composition. In the move towards sustainability, finding and implementing ways to recycle batteries is on the horizon as well; burgeoning techniques include the upcycling or rejuvenating of cathodes. With ever growing demand and changes in R&D, the ability to quantify materials in the low and sub ppb range will be critical as this industry looks towards the next generation of batteries.

Materials and Methods

Instrumentation

The samples discussed were all prepared for analysis using the BLADE microwave digestion system with iWave® temperature control. The BLADE provides sequential digestion of samples with automatic loading and unloading using a robotic arm. The system uses quartz vessels, with the option of Teflon® liners, and a two-piece snap cap. Samples are heated to temperature using microwave energy and stirred with stir bars to ensure even digestion. After digestion, samples are cooled, unloaded from the cavity, and the next sample is run following the same sequence until the entire queue is complete. The sequential format of the BLADE allows for a variety of acids to be used in a batch. During digestions, the samples can be observed using a built-in camera.

Sample Preparation

A 1000 mg/L custom multi-element standard from Inorganic Ventures was used to spike acid blanks at 20 ppm. All samples were prepared in triplicate with sample weights of 0.25 g. The samples for this study included SRMs, lithium sources, cathode materials, and anode material. Lithium ores petalite (NIST SRM 182) and lepidolite (NIST SRM 183) as well as Montana Soil II (NIST SRM 2711a) were used as validation samples. Lithium sources included an electrolyte, compounds, and minerals. The samples completely digested were lithium hexafluorophosphate ($LiPF_6$), lithium carbonate, and spodumene. The cathode materials were lithium nickel cobalt aluminum oxide (NCA), lithium iron phosphate (LFP), lithium manganese cobalt (NMC), and lithium cobalt oxide (LCO).

The anode material analyzed was graphite. The graphite sample was the only sample that was prepared using a high temperature leach.

A combination of acids and temperatures was used to optimize the digest conditions of these samples, listed in **Table 1** (page 3). All samples were run using the available TFM liner. For samples without the use of HF, a 1:1 ratio of water to acid could also be used in the BLADE quartz vessel (with or without liner).

Samples that needed HF required a second digestion step using boric acid to dissolve acid-insoluble fluorides such as CaF_2. After cooling below 70 °C, the vessels were opened, and 2.5 g of solid boric acid + 12 mL DI H_2O were added. The vessels were sealed, and the solutions were heated to 160 °C using the program outlined in the Boric Acid Neutralization BLADE Method Note. All samples were diluted to 50 g with DI water prior to anaysis.

Analysis

Samples were analyzed using an Agilent 5110 ICP-OES (Agilent Technologies, Santa Clara, CA). The conditions are listed in **Table 2** (page 3). Acid blanks as well as spiked acid blanks were utilized for verification of the analysis prior to sample analysis. All samples were analyzed for a range of trace and percentage-level metals, based upon their composition and associated contaminant concerns.

Results

Acid blank and spiked acid blank data are shown in **Table 3** (page 3). Analyte concentrations in the acid blanks, both with and without HF, were negligible or not detected and spiked blanks had recovery values between 95-105%. Upon validation of the spiked blanks and blank values, the rest of the samples were analyzed.

Percent recovery data for all SRMs digested with added HF are shown in **Table 4** (on page 3). Lithium recoveries for both the ore samples, petalite (SRM 182) and lepidolite (SRM 183), were greater than 95%. Montana Soil II (SRM 2711a) was chosen as a standard, as it is similar to an ore and is certified for a wide variety of elements. Recovery values were all above 90%. In comparison, recovery values for the same matrices but digested without HF are listed in **Table 5** (on page 4). Recovery values for this set of samples were more varied and lower overall.

The major and trace element data for lithium sources, $LiPF_6$, lithium carbonate, and spodumene are shown in **Table 6** (on page 4), and the major constituents percent in **Table 7** (on page 4). The mass faction % gave the expected ratios.

For the cathode materials and anode material tested, **Table 6** lists the recoveries of trace elements and major elements found in the anode and cathode materials. Understanding which elements are present and finding ways to reduce elemental impurities will be necessary to improve the performance in future batteries. Furthermore, the major constituents mass fraction % calculated from **Table 7** gave comparable ratios to previously reported MARS 6 data.

Conclusion

The proper determination of the elemental composition of batteries is crucial. Given the constant design changes and the increased push towards sustainability, the need for battery testing and quality control has never been greater. Proper sample preparation providing homogeneous solutions for analysis plays a vital role in this process, whether it be for new developments or greener initiatives. The BLADE with iWave® temperature control was able to digest a variety of source materials as well as anode and cathode materials. The digestion conditions resulted in clear and particle-free solutions for all of the samples digested while leached graphite indicated acceptable recovery. Comparisons in preparations involving the use of HF showed increased recoveries versus not using HF. The compositions of the cathode materials were found to be consistent with data collected via digestion on the MARS 6. Since the BLADE digests one sample at a time, compared to the batch format of the MARS 6, the BLADE methods are more amenable to rush samples and rapid method optimization. In addition, the BLADE methods often use less acid in comparison and can be shorter in time to complete a run. Recoveries for both SRMs and actual samples show microwave digestion on either the BLADE or MARS 6 as great options for preparing these types of samples.

Table 1. Sample with Acid Mixtures and Temperature Conditions

Sample	Material Type	Acid Mixture	Temperature
Montana Soil II (SRM 2711a)	NIST SRM	(1:1) $HCl:H_2O$	220
		(1:1) $HCl:H_2O$ + 5 mL HF	220
Petalite (SRM 182)	NIST SRM	(1:1) $HCl:H_2O$	220
		(1:1) $HCl:H_2O$ + 5 mL HF	220
Lepidolite (SRM 183)	NIST SRM	(1:1) $HCl:H_2O$	220
		(1:1) $HCl:H_2O$ + 5 mL HF	220
$LiPF_6$	Lithium Source	(3:1) $HCl:HNO_3$	210
Lithium Carbonate	Lithium Source	(1:1) $HNO_3:H_2O$	200
Spodumene	Lithium Source	(1:1) $HCl:H_2O$	220
LFP	Cathode	(3:1) $HCl:HNO_3$	225
NCA	Cathode	(7:3) $HCl:H_2O$	220
NMC	Cathode	(9:1) $HNO_3:HCl$	210
LCO	Cathode	(9:1) $HNO_3:HCl$	210
Graphite	Anode	(3:1) $HCl:HNO_3$	225

Table 2. Instrument Conditions of Agilent 5110 ICP-OES

Parameters	Values
RF Power (kW)	1.2
Viewing Mode	SVDV
Viewing Height (mm)	8
Nebulizer Flow (L/min)	0.70
Plasma Flow (L/min)	12.00
Aux Flow (L/min)	1.00
Rinse (sec)	30
Internal Standard	Yttrium (377.433 nm)
Background Correction	Fitted

Table 3. PPB Recoveries of Acid Blanks and Percent Recoveries of Spiked Acid Blanks (n=3)

Acid Blank	Al	Ca	Co	Fe	K	Li	Mn	Na	P	Se	Si	Ti	V	Zn
(1:1) HCl:H_2O	0.00333	n.d.	n.d.	n.d.	0.253	n.d.	n.d.	n.d.	n.d.	n.d.	0.00333	n.d.	n.d.	n.d.
(1:1) HCl:H_2O + 5 mL HF	0.290	0.100	n.d.	0.0350	0.350	n.d.	n.d.	0.990	0.0700	0.0950	5.46	n.d.	0.0300	n.d.
20 ppm Spike in 1:1 HCl:H_2O	96.5	96.6	97.7	97.5	102	96.5	97.2	100.	99.3	97.5	97.5	96.9	95.7	96.4

Table 4. Percent Recoveries of NIST SRM Materials Montana Soil II*, Petalite and Lepidolite using HF (n=3)

Sample	Al	Ca	Co	Fe	K	Li	Mn	Na	Ni	P	Si	Ti	V	Zn
SRM 2711a	90.8	90.5	94.7	96.6	95.5	*	94.0	105	93.9	92.1	90.4	95.1	99.9	92.6
SRM 182						101								
SRM 183						95.2								

*Montana Soil II (SRM 2711a) is not certified for Li.

Table 5. Percent Recoveries of NIST SRM Materials Montana Soil II*, Petalite and Lepidolite without using HF (n=3)

Sample	Al	Ca	Co	Fe	K	Li	Mn	Na	Ni	P	Si	Ti	V	Zn
SRM 2711a	47.8	65.9	90.1	86.1	35.3	*	81.9	8.04	73.3	87.3	0.591	58.4	81.5	90.0
SRM 182						8.20								
SRM 183						83.6								

*Montana Soil II (SRM 2711a) is not certified for Li.

Table 6. PPM Recoveries for Elemental Impurities and Major Elements in Lithium Sources, Cathode, and Anode Materials (n=3)

	Major and Trace Elements [ppm]												
	Material Type	**Al**	**Ca**	**Co**	**Fe**	**K**	**Mn**	**Na**	**Ni**	**P**	**Si**	**Ti**	**V**	**Zn**
$LiPF_6$	Lithium Source	4.06	1.02	0.0367	13.5	3.38	0.0767	137	8.00	2.07E5	4890	0.0933	0.210	1.06
Lithium Carbonate	Lithum Source	n.d.	2.54	0.750	0.253	91.4	n.d.	10.1	0.560	0.643	n.d.	n.d.	0.0233	n.d.
Spodumene	Lithum Source	1.31E5	437	8.79	1230	3940	426	2820	3.43	660	3.00E5	83.8	6.28	16.9
NCA	Cathode	1.00E4	30.2	8.52E4	12.2	20.3	80.3	2.90	4.75E5	90.3	1350	0.450	4.50	27.3
LFP	Cathode	99.6	12.1	6.55	3.67E5	18.8	74.5	176	14.6	2.00E5	27.5	1.70E3	8.24	8.73
NMC	Cathode	62.2	7.62	6.65E4	2.53	56.3	3.34E4	61.8	4.75E5	9.53	1.03E3	0.00333	0.0300	24.0
LCO	Cathode	45.5	39.0	6.14E5	27.1	64.9	4.65	123	9.69	8.29	8.86E4	827	1.98	1.89
Graphite	Anode	0.347	2.29	1.72	110	17.7	0.00667	60.3	7.98	20.1	3.23E4	7.16	6.50	n.d.

Table 7. Major Constituents Recoveries in the Cathode Materials and Lithium Sources

		Major Constituents [%]								
		Li	**Ni**	**Co**	**Al**	**Fe**	**Ti**	**P**	**Mn**	**Si**
$LiPF_6$	BLADE	4.62						20.7		
Lithium Carbonate	BLADE	17.9								
Spodumene	BLADE	3.72			13.1					30.0
NCA	BLADE	5.55	47.5	8.52	1.00					
	MARS 6	5.65	47.5	8.46	1.04					
LFP	BLADE	3.87				36.7	0.166	20.0		
	MARS 6	4.12				33.0	0.182	20.5		
NMC	BLADE	6.04	47.5	6.65					3.34	
	MARS 6	6.09	47.8	6.73					3.42	
LCO	BLADE	6.72		61.4						
	MARS 6	7.27		61.0						

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