

# Sample Preparation and Analysis of Materials Used in Lithium Battery Production

## Abstract

Lithium ion batteries travel with us everywhere, everyday, all the time. From our phones, to our laptops, to even nowadays our watches and vehicles, these energy sources have become an integral part of our lives. Demand for lithium and other metals needed for the production of lithium batteries continues to accelerate. Determining the purity of the anode and cathode materials, as well as the lithium sources, is crucial. CEM has developed digestion protocols that can either provide a total digest or more efficiently extract elements from these samples. The higher temperatures achieved by microwave digestion provide more aggressive conditions as compared to hot block heating. This results in a more accurate trace metals analysis, which is critical for this industry. Lithium ores, salts, cathode and anode materials, and a recycled cathode material were sourced, digested, and analyzed. Samples were digested in triplicate, and SRMs and spikes were used to validate both digestion and analysis.

## Introduction

Lithium has been called the white gold of electric vehicles. The lithium battery industry was first developed in the 1960s by NASA. In 1985, Akira Yoshino, a Japanese Chemist, implemented petroleum coke into the composition of the design, which resulted in a more stable and safer version of lithium ion battery technology. The U.S. was the leading supplier of lithium until the 1990s. But today, the U.S. is far behind, with only 1% of global lithium being mined and processed in the U.S., according to the U.S. Geological Survey. The U.S. holds almost 8 million metric tons in reserve, ranking it among the top five countries in the world, but there is only one major operating lithium mine in the U.S., Albemarle's Silver Peak in Nevada. However, many more projects are in the works. Exploration in California, Nevada, Utah, and Arizona is very likely for the foreseeable future. Ancient dry lake beds are the best sources of lithium salts. Many parts of the Great Basin and Southwest are covered with these lake beds and they hold great potential for lithium.

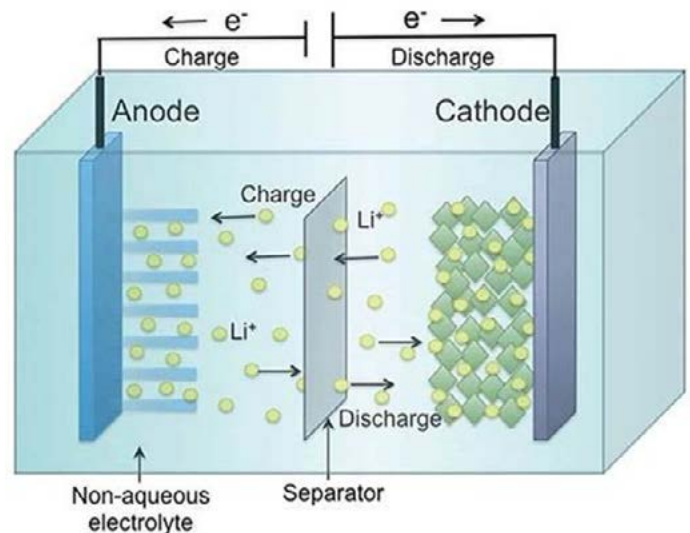
Continental brines provide approximately three-fourths of the world's lithium production, due to their relatively low production costs. These brines are a combination of salts, which include sodium and potassium. It is well documented that sodium can cause batteries to overheat and even catch fire, which is a safety issue.

Other metal impurities can lead to decreased performance. In order for battery technology to continue to improve, scientists and engineers must have better control of the composition of the raw materials, as well as intermediate and finished products. This will involve additional metals testing at lower detection limits.

## Materials and Methods

### Battery Materials

A lithium ion battery (shown in **Figure 1**) has four major components; the anode, the cathode, an electrolyte solution, and separator. The anode is typically graphite-based and stores the lithium ions in the battery. The cathode is the energy source of the battery and is composed of lithium oxide doped with metal (or metals) to optimize the battery capacity output and lifetime. The most common cathode materials are Lithium Iron Phosphate (LFP), Lithium Nickel Manganese Cobalt Oxide (NMC), Lithium Cobalt Oxide (LCO), and Lithium Nickel Cobalt Aluminum Oxide (NCA). An electrolyte solution provides the medium to allow for migration of ions and is composed of salts, solvents, and other additives. Finally the separator is a special polymer barrier between the anode and cathode. Each of these requires trace metals analysis for impurities.



**Figure 1.** Lithium Ion Battery

## Instrumentation

A CEM MARS 6™ microwave digestion system with iWave® temperature technology (**Figure 2**) was used to prepare a variety of samples used in the production of lithium batteries. The iWave contactless temperature measurement system provides an accurate and simple way to control the temperature of every vessel to insure proper digestion conditions are met. The Easy Prep vessel was chosen as it could achieve the temperature requirements for all digestions. Samples were analyzed on an Agilent 5110 ICP-OES (Agilent Technologies, Santa Clara, CA).



**Figure 2.** MARS 6 with EasyPrep Vessels

## Sample Preparation

Samples ranged from lithium ores and salts to anode and cathode materials. The lithium ores lepidolite (NIST SRM 183) and petalite (NIST SRM 182) were included to validate the ability to effectively extract and analyze lithium from the ore. A third SRM, Montana Soil II (NIST SRM 2711a), was also used to validate the digestion and analysis process of additional certified elements. Sample weights ranged from 0.25 to 0.5 grams. All samples were prepared in triplicate.

A combination of acids and temperatures were used to optimize the digestion conditions for these samples. They are listed in **Table 1** (page 3).

Samples that needed HF required a second digestion step using boric acid to dissolve acid-insoluble fluorides such as  $\text{CaF}_2$ . After cooling below 70 °C, the vessels were opened, and 2.5 g of solid boric acid + 20 mL  $\text{H}_2\text{O}$  were added. The vessels were sealed, and the solutions were heated to 170 °C using the following program:

Stage	Ramp (min)	Temp (°C)	Hold (min)	Power (W)
1	15:00	170	15:00	1800

## Analysis

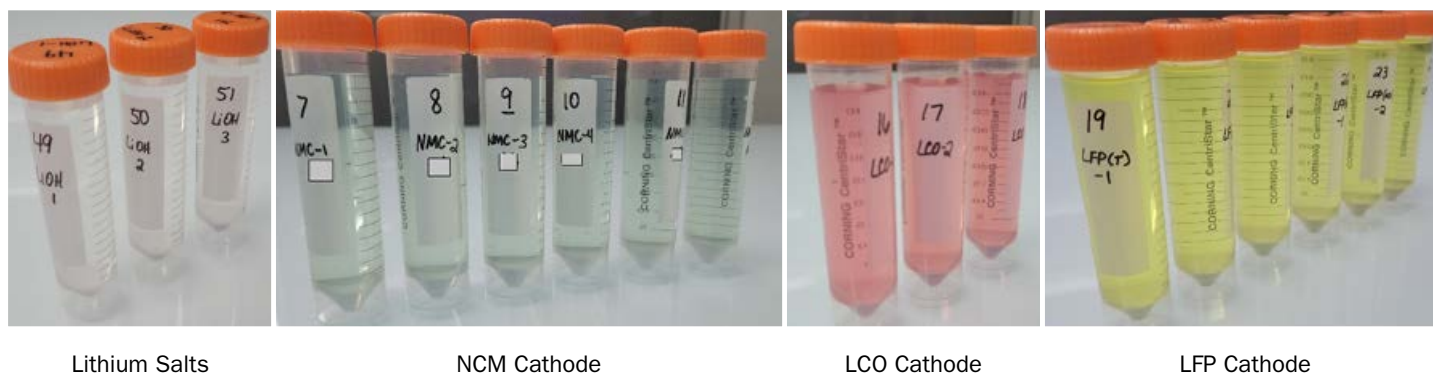
Samples were analyzed on an Agilent 5110 ICP-OES with conditions listed in **Table 2** (page 3). All samples were analyzed for a range of trace and percentage-level metals, based upon their composition and associated contaminant concerns.

## Results and Discussion

All samples other than LFP, anode, and recycled material provided clear digests. The anode material was filtered prior to analysis. All samples were diluted to 50 mL final volume or diluted to a final volume of 50 mL prior to analysis. Of note is that the lithium ores and salts provided clear solutions. The cathode materials provided clear and colored solutions based upon the ratio of the metals in the material. For example, these colors and intensities can indicate the potential ratios of the Ni to Co for NMC, as there are several formulations of NMC. See **Figure 3** for examples of the colors of varied digestion solutions.

Percent recovery data for all certified reference materials are shown in **Table 3** (page 3). Lithium recoveries for both of the ore samples, petalite (SRM 182) and lepidolite (SRM 183), are greater than 96%.

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.



**Figure 3.** Digested Samples After Dilution

Once again recoveries were excellent across the suite of elements.

In order to validate the analysis, lithium carbonate was spiked with a low spike at 1 ppm and a high spike at 20 ppm using multi-element standards. Recovery data is shown in **Table 4** (page 4) and all are in range of their spiked values, other than those elements naturally occurring in the lithium salt. Note the elevated potassium and sodium values, which are known impurities for lithium salts.

**Table 5** (page 4) lists the elemental impurities found in the anode and cathode materials. Understanding which elements are present and finding ways to reduce or eliminate them will be necessary to improve the performance in future batteries. **Table 6** (page 4) lists the major elements found in two of the cathode materials. This can be used to certify the amounts and ratios of various metals added to the cathode material.

## Conclusions

It is critical that manufacturers can identify the presence of impurities in lithium battery materials to ensure that there is no compromise in final battery performance. The industry is demanding better-performing batteries with a longer lifetime, which in turn calls for the use of higher-purity raw materials. Proper sample preparation providing homogeneous solutions for analysis plays a vital role in this process. The MARS 6 with iWave temperature control was able to digest a variety of samples for lithium battery production. The digestion conditions resulted in clear and particle-free solutions for all of the cathode materials and lithium-based salts, while providing a consistent aggressive leach for the anode material. Recoveries for both SRMs and actual samples show microwave digestion is the best option for preparing these types of samples. Future work will involve preparing samples without HF to provide a comparison of results as many labs avoid this acid.

**Table 1.** Samples with Acid Mixtures and Temperature Conditions

Sample	Material Type	Acid Mixture	Temperature
Spodumene	Lithium Source	(1:1) HCl:H <sub>2</sub> O + 5 mL HF	210°C
Montana Soil II (SRM 2711a)	Lithium Source	(1:1) HCl:H <sub>2</sub> O + 5 mL HF	210°C
Petalite (SRM 182)	Lithium Source	(1:1) HCl:H <sub>2</sub> O + 5 mL HF	210°C
Lepidolite (SRM 183)	Lithium Source	(1:1) HCl:H <sub>2</sub> O + 5 mL HF	210°C
Lithium Hydroxide	Lithium Source	(1:1) HNO <sub>3</sub> :H <sub>2</sub> O	180°C
Lithium Carbonate	Lithium Source	(1:1) HNO <sub>3</sub> :H <sub>2</sub> O	180°C
LFP	Cathode	(3:1) HCl:HNO <sub>3</sub>	220°C
NMC	Cathode	(9:1) HNO <sub>3</sub> :HCl	210°C
LCO	Cathode	(9:1) HNO <sub>3</sub> :HCl	210°C
NCA	Cathode	(1:1) HCl:H <sub>2</sub> O	230°C
Graphite	Anode	(3:1) HCl:HNO <sub>3</sub>	220°C

**Table 2.** Instrument Conditions of Agilent 5110 ICP-OES

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

**Table 3.** Percent Recoveries of NIST SRM Materials Montana Soil II\*, Petalite and Lepidolite

Sample	Al	Ca	Co	Fe	K	Li	Mn	Na	P	Si	Ti	V	Zn
SRM 2711a	93.3	92.9	101	94.8	102	*	95.8	108	101	96.6	98.9	97.8	96.8
SRM 182						99.7							
SRM 183						96.4							

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

**Table 4.** Percent Recoveries of Spiked Lithium Carbonate – Low Spike 1 ppm and High Spike 20 ppm

Low Spike - Lithium Carbonate - Spike Recovery														
Sample	Al	Ca	Co	Fe	K	Li	Mn	Na	P	Se	Si	Ti	V	Zn
Lithium Carbonate LS	1.16	0.99	0.997	1.02	4.32	816.30	1.02	1.76	1.15	1.16	1.16	1.07	1.03	1.00
Actual	1	1	1	1	1	1	1	1	1	1	1	1	1	1
% Recovery	116	99.0	99.7	102	432	81630	102	176	115	116	116	107	103	100
High Spike - Lithium Carbonate - Spike Recovery														
Sample	Al	Ca	Co	Fe	K	Li	Mn	Na	P	Se	Si	Ti	V	Zn
Lithium Carbonate HS	22.6	19.1	19.3	19.8	35.6	828.4	20.0	25.4	22.2	22.3	21.8	20.2	20.0	19.9
Actual	20	20	20	20	20	20	20	20	20	20	20	20	20	20
% Recovery	113	95.5	96.5	98.8	178	4142	100	127	111	111	109	101	100.0	99.6

**Table 5.** PPM Recoveries for Elemental Impurities and Major Elements (n=3)

Sample	Spodumene	NCA	NMC	LCO	LFP	Graphite
Al	131808.27	10364.28	16.71	48.80	53.90	3.08
Ca	667.34	35.47	1.93	53.06	<MDL	<MDL
Co	2.52	84566.15	70465.31	609466.91	14.43	2.46
Fe	1091.63	10.39	2.18	31.18	330221.51	93.03
K	3233.39	15.92	<MDL	<MDL	<MDL	<MDL
Mn	389.28	6.83	33889.97	13.23	501.20	2.40
Na	2311.48	<MDL	13.49	66.49	124.28	<MDL
P	650.71	84.79	<MDL	23.04	205006.98	<MDL
Se	80.24	0.97	42.12	112.26	3.13	1.42
Si	325989.38	<MDL	<MDL	<MDL	<MDL	<MDL
Ti	107.42	0.43	0.75	898.42	1822.48	7.99
V	1.08	5.75	4.43	2.85	11.43	7.27
Zn	11.78	17.46	26.48	<MDL	12.67	<MDL

**Table 6.** Percent Recoveries of Major Elements in NMC and LFP

Sample	Li	Ni	Mn	Co	Fe	P
NMC 811	7.56	55.98	3.39	7.05		
LFP	4.78				22.85	14.36

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