

Instrument: ONH836 Series

Determination of Oxygen in Lithium Battery Materials

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Introduction

Lithium-ion batteries typically use a lithium-based powder—such as lithium iron phosphate (LiFePO_4 or LFP) or lithium nickel manganese cobalt oxide (NMC)—as the cathode material, and a graphitic carbon electrode with a metallic backing as the anode. Lithium-based compounds have a layered (NMC) or olivine (LiFePO_4) crystalline structure that facilitates efficient diffusion of lithium-ions. LiFePO_4 offers good electrochemical performance, low resistance, and is one of the safest and most stable cathode materials available for lithium-ion batteries. While Li-NMC cathode materials provide improved energy density and power output, they can be less stable.

Determining the oxygen content in lithium battery materials is important because the oxygen content directly affects the structure, performance, stability, and safety of the cathode. In lithium-ion battery materials, the oxygen content is essential for peak performance, as deviations (specifically oxygen loss) result in the degradation of battery capacity, voltage, and safety. Monitoring oxygen levels in lithium battery materials throughout the production process is critical, as it enables manufacturers to confirm that the cathode material meets the required specifications for optimal battery performance and safety.

Instrument Model and Configuration

The O836 is designed for wide-range measurement of oxygen content. A pre-weighed sample is placed in a graphite crucible which is heated in an impulse furnace to release analyte gases. Oxygen present in the sample reacts with the graphite crucible to form CO and CO_2 . An inert gas carrier (helium) sweeps the liberated analyte gases out of the furnace, through a mass flow controller, and through a series of detectors. CO and CO_2 are detected using non-dispersive infrared (NDIR) cells. The gas then flows through a heated reagent where the CO is oxidized to form CO_2 . The gas continues through another NDIR cell where CO_2 is detected.

Sample Preparation

Samples should be a uniform, representative, powder or granular material. Samples should be analyzed as received.

Note: LECO Reference Materials typically do not require preparation prior to analysis. Refer to the preparation statement on the reference material certificate. Please reference the appropriate Safety Data Sheets (SDS) for safe handling of all reference materials and samples.



Accessories

776-247 Graphite Crucibles, 782-721 Lower Electrode Tip for 776-247 crucibles without automation, 618-376 Lower Electrode Tip for 776-247 crucibles with automation, 502-040 Tin Capsules, a Five-place Balance**, 766-053 Crucible Tweezers, and 760-138 Sample Tweezers.

****Due to the high oxygen levels in these materials and the generation of excessive dust, samples should be analyzed at a lower sample mass (0.005–0.01 g) to avoid excessive dust buildup and NDIR cell saturation. When weighing sample masses ≤ 0.05 g, a five-place balance is required.**

Reference Materials

LCRM®, LRM®, NIST, or other suitable reference materials.

Method Parameters[†]

General Parameters

Carrier Gas Type	Helium ^{††}
Sample Introduction	Automated Sample Drop
Analysis Delay	30 s
Auto Analyze on Mass Entry	No
Outgas Before Mass Entry	No
Outgas At End Of Analysis	No
Wait for User to Load Sample	Yes
Load Crucible After Analysis	No
Nominal Mass	1.0000 g
Vacuum On Time	25 s

^{††}Argon carrier gas is not suitable for this application.

Element Parameters

Integration Delay	0 s
Starting Baseline	2 s
Use Comparator	No
Integration Time	200 s
Use Endline	Yes
Ending Baseline	2 s
Range Select	High
Comparator Level	--
Minimum Integration Time	--
Maximum Integration Time	--

Furnace Parameters

Furnace Control Mode	Power
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Outgas Parameters

Cycles	2
Power Mode	Constant
Power	5500 [†] W
Time	15 s
Cool Time	5 s

Surface Oxide Removal Parameters

Remove Surface Oxide	No
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Analyze Furnace Settings

Step 1	Power Mode	Ramped
	Low Power	1200 [†] W
	High Power	2500 [†] W
	Time	150 s
Step 2	Power Mode	Ramped
	Low Power	2500 [†] W
	High Power	4900 [†] W
	Time	50 s

[†]Refer to the 836 Series Operator's Instruction Manual for parameter definitions.

[‡]May vary based on the line voltage. Adjust to improve recovery or reduce crucible burn-through.

Procedure

1. Prepare the instrument as outlined in the operator's instruction manual.
2. Determine the instrument blank.
 - a. From the Analysis Screen, use the Login Bar to add three or more blank replicates.
 - b. Press the Analyze button on the Analysis screen. After a short delay, the loading head slide-block will open.
 - c. Place a 502-040 Tin Capsule into the open port at the top of the loading head. Leave the capsule open to avoid trapping atmosphere.
 - d. Press the Analyze button on the Analysis screen again. The loading head slide-block will close, and the lower electrode will open.
 - e. Clean the upper and lower electrodes manually or with an equipped automatic cleaner.
 - f. Firmly place a 776-247 Graphite Crucible on the lower electrode tip.
 - g. Press the Analyze button on the Analysis screen. The lower electrode will close, and the analysis sequence will start and end automatically.
 - h. Perform steps 2b through 2g a minimum of three times.
 - i. Set the blank following the procedure outlined in the operator's instruction manual.
3. Calibrate or drift correct.
 - a. From the Analysis Screen, use the Login Bar to add three or more replicates for each calibration/drift material being utilized.
 - b. Weigh an appropriate mass of a suitable reference material into a 502-040 Tin Capsule and enter the mass and sample identification into the appropriate replicate fields in the Analysis Screen.
 - c. Press the Analyze button on the Analysis screen. After a short delay, the loading head slide-block will open.

- d. Place the tin capsule containing the calibration/drift material into the open port at the top of the loading head. Leave the capsule open to avoid trapping atmosphere.
 - e. Press the Analyze button on the Analysis screen again. The loading head slide-block will close, and the lower electrode will open.
 - f. Clean the upper and lower electrodes either manually, or with an equipped automatic cleaner.
 - g. Firmly place a 776-247 Graphite Crucible on the lower electrode tip.
 - h. Press the Analyze button on the Analysis Screen. The lower electrode will close, and the analysis sequence will start and end automatically.
 - i. Perform steps 3b through 3h a minimum of three times for each calibration/drift sample utilized.
 - j. Calibrate/drift following the procedure outlined in the operator's instruction manual.
 - k. Verify the calibration by analyzing several replicates of an appropriate mass of another/different calibration/drift material, following steps 3b through 3h, and verify that the results are within the tolerance range.
4. Analyze the samples.
 - a. From the Analysis Screen, use the Login Bar to add the desired number of sample replicates.
 - b. Weigh an appropriate mass (~ 0.005 – 0.01 g) of a sample into a 502-040 Tin Capsule and enter the mass and sample identification into the appropriate replicate fields in the Analysis Screen.
 - c. Press the Analyze button on the instrument screen. After a short delay, the loading head slide-block will open.
 - d. Place the tin capsule containing the sample into the open port at the top of the loading head. Leave the capsule open to avoid trapping atmosphere.
 - e. Press the Analyze button on the instrument screen again. The loading head slide-block will close, and the lower electrode will open.
 - f. Clean the upper and lower electrodes either manually, or with an equipped automatic cleaner.
 - g. Firmly place a 776-247 Graphite Crucible on the lower electrode tip.
 - h. Press the Analyze button on the Analysis screen. The lower electrode will close, and the analysis sequence will start and end automatically.
 - i. Perform steps 4b through 4h for each sample to be analyzed.

Typical Results

Results are based on a linear, force through origin calibration utilizing BAM-SO14 Li-NMC Cathode Material (34.0 % O). The calibration was verified using LECO 502-702 (Lot: 1000) Iron Powder LCRM (1.10 % O).

Sample	Mass (g) ^{††}	Oxygen (%)
Lithium Iron Phosphate (LiFePO₄)	0.00495	40.3
MSE Supplies (PO0127)	0.00487	39.5
	0.00471	40.5
	0.00488	40.8
	0.00500	39.7
	$\bar{x}$ =	40.2
	s =	0.5
Lithium Nickel Manganese Cobalt Oxide	0.00991	32.7
(Li-NMC Oxide)	0.00999	32.6
Sigma Aldrich (761001)	0.01007	34.9
	0.00984	35.0
	0.01024	33.2
	$\bar{x}$ =	33.7
	s =	1.2
Lithium Manganese Nickel Oxide	0.01009	33.4
(Li-NMO)	0.01005	33.9
Sigma Aldrich (915432)	0.01003	34.3
	0.01009	33.2
	0.01006	32.8
	$\bar{x}$ =	33.5
	s =	0.6

$\bar{x}$ = Sample Mean; s = Sample Standard Deviation

^{††}A five-place balance was used to weigh all samples.