

Instrument: CS844 Series

Determination of Carbon and Sulfur in Lithium Iron Phosphate Battery Materials

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Introduction

Lithium Iron Phosphate batteries are a type of Lithium-ion battery that uses Lithium Iron Phosphate (LiFePO_4) powder as the cathode material and a graphitic Carbon electrode with a metallic backing as the anode. Lithium Iron Phosphate, also called LFP, is a crystalline, grey-to-black powder with an olivine crystal structure. This unique crystal structure facilitates efficient diffusion of Lithium-ions. Lithium Iron Phosphate offers good electrochemical performance, low resistance, and is one of the safest and most stable cathode materials available for Lithium-ion batteries.

Carbon determination in LiFePO_4 is important as the Carbon content directly impacts the performance of this battery material. In addition, emerging battery technologies can take advantage of improved Sulfur utilization when LiFePO_4 is used as an additive, making Sulfur determination in the base material an important quality control procedure.

Instrument Model and Configuration

The LECO CS844 is a combustion analyzer that utilizes an induction furnace for the rapid, simultaneous determination of Carbon and Sulfur using non-dispersive infrared (NDIR) cells. A pre-weighed sample is combusted in a stream of Oxygen using RF induction to heat the sample. Carbon and Sulfur present in the sample are oxidized to Carbon Dioxide (CO_2) and Sulfur Dioxide (SO_2) and swept by the Oxygen carrier through a heated dust filter, a drying reagent, and then through two non-dispersive infrared (NDIR) cells, where Sulfur is detected as SO_2 . The gas flow continues past a heated catalyst where Carbon Monoxide (CO) is converted to CO_2 and where SO_2 is converted to Sulfur Trioxide (SO_3), which is subsequently removed by a filter. Carbon is then detected as CO_2 by a second pair of NDIR cells.

NDIR cells function on the principle that CO_2 and SO_2 absorb infrared (IR) energy at unique wavelengths within the IR spectrum. Incident IR energy at these wavelengths is absorbed as the analyte gases pass through the IR absorption cells. Because absorption is dependent upon the path length, short and long path-length IR cells are provided for measurement of high- and low-range signals. The software automatically selects which cell to use for optimum measurement.

Method Summary

Two different methods were utilized for the generation of data included in this application note. The first approach outlines a method for simultaneous Carbon and Sulfur determination using 502-173 LECOCEL II HP and 502-231 HP Iron Chip Accelerators. Due to the low Sulfur levels often found in LiFePO_4 , a second method was designed to



produce a lower Sulfur blank value resulting in an improved lower method detection limit for Sulfur. The second approach outlines a method for Sulfur-only determination using 763-266 LECOCEL, 501-078 Iron Powder, and 501-636-HAZ Vanadium Pentoxide (V_2O_5) accelerators. The second method is for Sulfur-only determination because the use of Iron Powder and Vanadium Pentoxide results in a higher Carbon blank value, therefore limiting the lower detection capabilities for Carbon. Vanadium Pentoxide is considered a hazardous material; therefore, proper precautions should be taken when handling this material.

Sample Preparation

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

Accessories

Method 1: Carbon and Sulfur Determination

528-018 or 528-018HP Ceramic Crucibles*, 502-173 LECOCEL II HP, 502-231 HP Iron Chip Accelerator, 773-579 Metal Scoop, and 761-929 Tongs.

Method 2: Sulfur-Only Determination

528-018 or 528-018HP Ceramic Crucibles*, 763-266 LECOCEL, 501-078 Iron Powder, 501-636-HAZ Vanadium Pentoxide (V_2O_5), 773-579 Metal Scoop, and 761-929 Tongs.

*For optimal precision, ceramic crucibles should be heated in a muffle or tube furnace (such as a LECO TF4) at 1350 °C for a minimum of twenty minutes. The crucibles should be removed from the furnace, allowed to cool for one to two minutes, and then transferred to a desiccator for storage until use. Crucibles should be reheated if not used within four hours. After baking, handle ceramic crucibles with clean tongs only; do not use fingers.

Reference Materials

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

General Parameters**

Parameter	
Purge Time	10 s
Delay Time	20 s
Sample Cool Time	0 s
Furnace Mode	Constant
Furnace Power	100 %
Nominal Mass	1.0000 g

Element Parameters**

Parameter	Carbon	Sulfur
Integration Delay	0 s	0 s
Starting Baseline	2 s	2 s
Use Comparator	No	No
Integration Time	55 s	65 s
Use Endline	Yes	Yes
Ending Baseline	2 s	2 s
Range Select	Auto	Auto
Range Lower Limit	850	850
Range Upper Limit	1000	1000

**Refer to CS844 Operator's Instruction Manual for parameter definitions.

Procedure

Method 1: Carbon and Sulfur Determination

1. Prepare the instrument for operation as outlined in the operator's instruction manual.
2. Determine Blank.
 - a. From the Analysis screen, use the Login bar to add five or more blank replicates.
 - b. Add ~1.2 g (1 scoop) of 502-173 LECOCEL II HP and ~0.8 g (1 scoop) of 502-231 HP Iron Chip Accelerator to a preheated 528-018HP Ceramic Crucible.
 - c. Place the crucible on the furnace pedestal, or in the appropriate autoloader position (if applicable) and initiate the analysis sequence.
 - d. Perform steps 2b through 2c a minimum of five times.
 - e. Set the blank following the procedure outlined in the operator's instruction manual.
3. Calibrate/Drift Correct.
 - a. From the Analysis screen, use the Login bar to add three or more standard/drift replicates.
 - b. Weigh an appropriate mass of a suitable reference material into a preheated 528-018HP Ceramic Crucible.
 - c. Enter the reference material mass and identification into the Analysis screen.
 - d. Add ~1.2 g (1 scoop) of 502-173 LECOCEL II HP to the crucible, covering the reference material.
 - e. Add ~0.8 g (1 scoop) of 502-231 HP Iron Chip Accelerator to the crucible, covering the reference material and the LECOCEL II HP.
 - f. Place the crucible on the furnace pedestal, or in the appropriate autoloader position (if applicable) and initiate the analysis sequence.
 - g. Perform steps 3b through 3f a minimum of three times for each reference material utilized.
 - h. Calibrate/Drift Correct following the procedure outlined in the operator's instruction manual.
 - i. Verify the calibration/drift correction by analyzing an appropriate mass of another/different suitable reference material, following steps 3b through 3f, and confirm that the results are within the acceptable tolerance range.
4. Sample Analysis.
 - a. From the Analysis screen, use the Login bar to add the desired number of sample replicates.
 - b. Weigh ~0.25 g of sample into a preheated 528-018HP Ceramic Crucible.
 - c. Enter the sample mass and identification into the Analysis screen.
 - d. Add ~1.2 g (1 scoop) of 502-173 LECOCEL II HP to the crucible, covering the sample.
 - e. Add ~0.8 g (1 scoop) of 502-231 HP Iron Chip Accelerator to the crucible, covering the sample and the LECOCEL II HP.

- f. Place the crucible on the furnace pedestal or in the appropriate autoloader position (if applicable) and initiate the analysis sequence.
- g. Perform steps 4b through 4f for each sample replicate being analyzed.

Method 2: Sulfur-Only Determination

1. Prepare the instrument for operation as outlined in the operator's instruction manual.
2. Determine Blank.
 - a. From the Analysis screen, use the Login bar to add five or more blank replicates.
 - b. Add ~0.4 g of 501-078 HP Iron Powder to a preheated 528-018HP Ceramic Crucible.
 - c. Tare the balance and add ~0.6 g of 501-636-HAZ Vanadium Pentoxide (V_2O_5) to the ceramic crucible and mix thoroughly with the Iron Powder.
 - d. Tare the balance again and add ~1.2 g (1 scoop) of 763-266 LECOCEL to the ceramic crucible, covering the Vanadium Pentoxide and Iron Powder mixture.
 - e. Place the crucible on the furnace pedestal, or in the appropriate autoloader position (if applicable) and initiate the analysis sequence.
 - f. Perform steps 2b through 2e a minimum of five times.
 - g. Set the blank following the procedure outlined in the operator's instruction manual.
3. Calibrate/Drift Correct.
 - a. From the Analysis screen, use the Login bar to add three or more standard/drift replicates.
 - b. Add ~0.4 g of 501-078 HP Iron Powder to a preheated 528-018HP Ceramic Crucible.
 - c. Tare the balance and add ~0.6 g of 501-636-HAZ Vanadium Pentoxide (V_2O_5) to the ceramic crucible and mix thoroughly with the Iron Powder.
 - d. Tare the balance again and weigh an appropriate mass of a suitable reference material to the ceramic crucible and mix thoroughly with the Iron Powder and Vanadium Pentoxide mixture.
 - e. Enter the reference material mass and identification into the Analysis screen.
 - f. Tare the balance again and add ~1.2 g (1 scoop) of 763-266 LECOCEL to the ceramic crucible, covering the reference material, Iron Powder, and Vanadium Pentoxide mixture.
 - g. Place the crucible on the furnace pedestal, or in the appropriate autoloader position (if applicable) and initiate the analysis sequence.
 - h. Perform steps 3b through 3g a minimum of three times for each reference material utilized.
 - i. Calibrate/Drift Correct following the procedure outlined in the operator's instruction manual.
 - j. Verify the calibration/drift correction by analyzing an appropriate mass of another/different suitable reference material, following steps 3b through 3g, and confirm that the results are within the acceptable tolerance range.
4. Sample Analysis.
 - a. From the Analysis screen, use the Login bar to add the desired number of sample replicates.
 - b. Add ~0.4 g of 501-078 HP Iron Powder to a preheated 528-018HP Ceramic Crucible.

- c. Tare the balance and add ~0.6 g of 501-636-HAZ Vanadium Pentoxide (V_2O_5) to the ceramic crucible and mix thoroughly with the Iron Powder.
- d. Tare the balance again and weigh ~0.25 g of sample to the ceramic crucible and mix thoroughly with the Iron Powder and Vanadium Pentoxide mixture.
- e. Enter the sample mass and identification into the Analysis screen.
- f. Tare the balance again and add ~1.2 g (1 scoop) of 763-266 LECOCEL to the ceramic crucible, covering the sample, Iron Powder and Vanadium Pentoxide mixture.
- g. Place the crucible on the furnace pedestal, or in the appropriate autoloader position (if applicable) and initiate the analysis sequence.
- h. Perform steps 4b through 4g for each sample replicate being analyzed.

Typical Results

Data was generated utilizing a linear, force through origin calibration for low Carbon and Sulfur ranges, and a linear, full regression calibration for high Carbon and Sulfur ranges using LECO 502-914 (Lot 1004) LCRM Synthetic Carbon and Sulfur (0.99 % C, 0.97 % S), LECO 502-905 (Lot 1003) LCRM Synthetic Carbon (5.00 % C), and LECO 502-964 (Lot 1001) LCRM Synthetic Carbon and Sulfur (0.12 % C, 0.10 % S). The calibration was verified using LECO 502-999 (Lot 1000) LCRM Steel Chip (0.0021 % C, 0.0012 % S). Samples for Carbon and Sulfur determination (method 1) were analyzed using 528-018HP Ceramic Crucibles, ~1.2 g 502-173 LECOCEL II HP, and ~0.8 g 502-231 HP Iron Chip Accelerator. Samples for Sulfur-only determination (method 2) were analyzed using 528-018HP Ceramic Crucibles, ~0.4 g 501-078 Iron Powder, ~0.6 g 501-636-HAZ Vanadium Pentoxide (V_2O_5), and ~1.2 g 763-266 LECOCEL.

Method 1: Carbon and Sulfur Determination

Samples [†]	Mass (g)	Carbon (%)	Sulfur (%)
LiFePO₄ Sample 1	0.2510	0.0034	<0.0010 ^{††}
Sigma-Aldrich	0.2501	0.0032	<0.0010 ^{††}
Part Number: 759546	0.2567	0.0028	<0.0010 ^{††}
	0.2518	0.0033	<0.0010 ^{††}
	0.2521	0.0031	<0.0010 ^{††}
	\bar{x} =	0.0032	--
	s =	0.0002	--
LiFePO₄ Sample 2	0.2511	1.1354	0.0136
	0.2563	1.1353	0.0144
	0.2511	1.1291	0.0139
	0.2552	1.1355	0.0142
	0.2540	1.1348	0.0139
	\bar{x} =	1.1341	0.0140
	s =	0.0028	0.0003
LiFePO₄ Sample 3	0.2612	1.3192	0.0175
MSE Supplies	0.2567	1.3166	0.0176
Part Number: PO0127	0.2611	1.3149	0.0177
	0.2526	1.3094	0.0179
	0.2542	1.3067	0.0185
	\bar{x} =	1.3134	0.0178
	s =	0.0052	0.0004

Method 2: Sulfur-Only Determination

Samples [†]	Mass (g)	Sulfur (%)
LiFePO₄ Sample 1	0.2536	<0.0003 ^{††}
Sigma-Aldrich	0.2531	<0.0003 ^{††}
Part Number: 759546	0.2542	<0.0003 ^{††}
	0.2551	<0.0003 ^{††}
	0.2585	<0.0003 ^{††}
	\bar{x} =	--
	s =	--
LiFePO₄ Sample 2	0.2502	0.0138
	0.2543	0.0134
	0.2506	0.0133
	0.2537	0.0133
	0.2552	0.0133
	\bar{x} =	0.0134
	s =	0.0002
LiFePO₄ Sample 3	0.2575	0.0170
MSE Supplies	0.2633	0.0167
Part Number: PO0127	0.2591	0.0168
	0.2617	0.0170
	0.2582	0.0171
	\bar{x} =	0.0169
	s =	0.0001

[†]Sulfur gettering has been observed in certain Lithium based materials such as Lithium Carbonate, which can cause low biased Sulfur results. A spike recovery test was performed to determine whether Sulfur gettering occurred during the analysis of Lithium Iron Phosphate. The results of this testing demonstrated that Sulfur gettering was not observed during the analysis of these materials.

^{††}Results were below the lower method detection limit.

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