Application Note

Instrument: CS744 Series

EMPOWERING RESULTS
Elemental Analysis | GC Mass Spectrometry | Metallography

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 CS744 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 drying reagent and then through a non-dispersive infrared (NDIR) cell, 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 another NDIR cell.

Sample Preparation

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

Accessories

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

**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 20 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 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	50 s	65 s
Use Endline	Yes	Yes
Ending Baseline	2 s	2 s

***Refer to CS744 Operator's Instruction Manual for Parameter definitions.*

Procedure

1. Prepare the instrument for operation as outlined in the operator's instruction manual.
2. Determine Blank.
   a. Login a minimum of three 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 three times.
   e. Set the blank following the procedure outlined in the operator's instruction manual.
3. Calibrate/Drift Correct.
   a. Login a minimum of three 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 Login 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 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. Login a sample with the desired number of replicates.
   b. Weigh ~0.25 g of sample into a preheated 528-018HP Ceramic Crucible.
   c. Enter the sample mass and identification into the Login 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 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.

*Typical Results**

Data was generated utilizing a linear, force through origin calibration using LECO 502-914 (Lot 1004) LCRM Synthetic Carbon and Sulfur (0.99% C, 0.97% S) and LECO 502-905 (Lot 1003) LCRM Synthetic Carbon (5.00% C). The calibration was verified using LECO 502-964 (Lot 1001) LCRM Synthetic Carbon and Sulfur (0.12% C, 0.10% S), and LECO 502-999 (Lot 1000) LCRM Steel Chip (0.0021% C, 0.0012% S). Samples were analyzed using 502-173 LECOCEL II HP, 502-231 HP Iron Chip Accelerator, and 528-018HP Ceramic Crucibles.

Samples	*Mass (g)*	*Carbon (%)*	*Sulfur (%)*
$LiFePO_4$† Sample 1	0.2519	0.0033	<0.0010††
Sigma-Aldrich	0.2553	0.0033	<0.0010††
PN: 759546	0.2530	0.0035	<0.0010††
	0.2531	0.0033	<0.0010††
	0.2538	0.0036	<0.0010††
	$\bar{x}$ =	**0.0034**	**--**
	s =	**0.0001**	**--**
$LiFePO_4$† Sample 2	0.2545	1.1302	0.0153
	0.2512	1.1299	0.0145
	0.2541	1.1438	0.0152
	0.2520	1.1381	0.0146
	0.2546	1.1370	0.0149
	$\bar{x}$ =	***1.1358***	***0.0149***
	s =	***0.0059***	***0.0004***
$LiFePO_4$† Sample 3	0.2530	1.3206	0.0175
MSE Supplies	0.2515	1.3227	0.0175
PN: PO0127	0.2515	1.3260	0.0174
	0.2556	1.3245	0.0181
	0.2525	1.3215	0.0176
	$\bar{x}$ =	***1.3231***	***0.0176***
	s =	***0.0022***	***0.0003***

†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

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