

Application Note AN-T-248

Lithium hydroxide and lithium carbonate in lithium hydroxide according to ISO/AWI 11045-1

Two-step lithium hydroxide titration with OMNIS

Lithium hydroxide monohydrate (LHM) is a preferred source of lithium for some of the high energy density cathode materials available on the market. Lithium carbonate impurities in LHM can lead to handling issues, inefficient processes during battery production, off-gassing effects, and other potential issues. As a result, the expectations and requirements for analytical test methods used to certify the quality of upstream materials have also increased. Titration test methods for lithium hydroxide and lithium carbonate impurity are key for monitoring and characterizing LHM product quality.

A two-step titration for lithium hydroxide and lithium carbonate according to ISO/AWI 11045-1 was performed in this study, resulting in fast, accurate determination of both lithium hydroxide and lithium carbonate in lithium hydroxide samples.

INTRODUCTION

As innovation drives increasing battery performance, purity requirements for upstream materials (such as lithium hydroxide monohydrate) have become more stringent. Lithium carbonate impurities in lithium hydroxide monohydrate can lead to issues with battery production, handling issues, and off-gassing effects. The expectations and requirements of analytical testing methods have increased in recent years. Accurate test methods for lithium hydroxide content and lithium carbonate impurity are essential for characterizing and monitoring the quality of lithium hydroxide monohydrate.

SAMPLE AND SAMPLE PREPARATION

This application is demonstrated on solid lithium hydroxide samples.

No sample preparation is required.

EXPERIMENTAL

The determinations are carried out on an OMNIS Sample Robot S with Dis-Cover lids (Figure 1), a nitrogen sparge source, a 907 Titrando, two 800 Dosinos, and an Ecotrode.

A 120 mL OMNIS beaker is sparged manually with nitrogen, then 1 g of sample is weighed into the titration beaker. The beaker is covered with a Dis-Cover cap and placed on the OMNIS Sample Robot S. The system adds 50 mL of nitrogen-sparged ultrapure water and titrates, under nitrogen, to pH 10.5 using 2 mol/L hydrochloric acid. Following this, the system titrates potentiometrically to two endpoints using 0.01 mol/L HCl.



Figure 1. An OMNIS Sample Robot S with Dis-Cover caps and nitrogen sparging helps to protect the lithium hydroxide samples from carbon dioxide absorption prior to analysis.

RESULTS

Repeatable results within the expected ranges were obtained for all the lithium hydroxide samples analyzed using this method (Table 1).

The first titration was a SET pH titration to pH 10.5 using 2 mol/L HCl. The second titration was a DET pH titration using 0.01 mol/L HCl. The two-step titration approach allows for efficient titration of the high lithium hydroxide content while still allowing for speciation of two endpoints (Figure 2). The first endpoint, plus the endpoint from the SET pH titration, corresponds to the lithium hydroxide content, while the second endpoint corresponds to the lithium carbonate content.

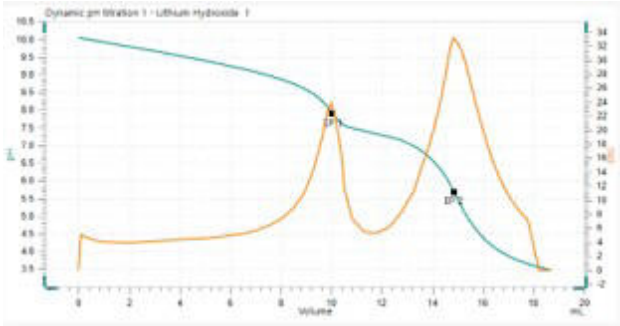


Figure 2. Lithium hydroxide and lithium carbonate endpoints from the second titration.

Table 1. Results of the determination of lithium hydroxide and lithium carbonate concentration in lithium hydroxide samples (n = 15).

Sample (n = 15)	Lithium hydroxide (%)	Lithium carbonate (%)
Mean value	58.36	0.27
SD(abs)	0.10	0.02
SD(rel) in %	0.17	6.15

CONCLUSION

The two-step titration approach using an OMNIS robot with Dis-Cover caps and nitrogen sparging allows for fast and accurate determination of both lithium hydroxide and lithium carbonate in lithium hydroxide samples. The initial SET pH titration with 2 mol/L HCl to reach pH 10.5 saves significant analysis time. The use of 0.01 mol/L HCl for the second titration allows for the speciation needed between the hydroxide and carbonate endpoints.

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CONFIGURATION



Main module Pick and Place S

Main module for setting up an OMNIS Sample Robot Pick&Place in size S. This module is comprised of module and rack plates. It is already equipped with the main lift and one gripper. In addition to sample racks and gripper fingers, workstations such as Pick&Place module or a pump module are required for using it to set up a functioning Sample Robot. The selection of these components proceeds in accordance with the application.



Pick and Place module

Module for installation in the module plate of the Pick&Place of the OMNIS Sample Robot. This workstation takes up the sample beaker for the analysis. Used sensors are cleaned or parked in the storage beaker of the Pick&Place module between analyses. If stirring is required during the analysis, then a separate rod stirrer must be used for this workstation.



Peristaltic (4-channel) pump module

Module for installation in the module plate of the Pick&Place of the OMNIS Sample Robot. This workstation is equipped with two rinsing pumps and two aspiration pumps each. They are used to clean the sensors in two Pick&Place modules and to empty the sample beaker after the analysis before it is placed back in the rack once again.



OMNIS Rod Stirrer Sample Robot

Rod stirrer with permanently mounted cable (2.5 m) for direct connection to the OMNIS Sample Robot.



Stirring propeller 20 mm ETFE

Stirring propeller, 20 mm, with adjustable height for use with Rod Stirrer "Titrator" or Rod Stirrer "Sample Robot"



Gripper fingers 43 - 65 mm

Gripper fingers for OMNIS Sample Robot Pick&Place for gripping sample beakers with an outer diameter of 43 to 65 mm.



Titration head 3xNS14 / 4x6.4 mm (P and P)

Titration head with 3 NS14 and 4x 6.4 mm openings for using 120 mL beakers in Pick&Place modules of the OMNIS Sample Robot Pick&Place with two retracted dosing tips. Prepared for being equipped with rinsing and aspiration tubing.



OMNIS sample rack, 16 x 120 mL, (PP)

OMNIS sample rack for OMNIS Sample Robot Pick&Place, suitable for 16 sample beakers. The following sample beakers can be used: 6.01400.200, 6.01400.300, 6.01400.303.
Plastic: Polypropylene (PP)



OMNIS sample rack, 16 x 120 mL, (PP)

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Plastic: Polypropylene (PP)



Sample beakers, clear glass, 120 mL, 20 pieces

Sample beakers, clear glass, 120 mL, suitable for 602041030 OMNIS sample rack, 20 pieces.



Sample beakers, clear glass, 120 mL, 20 pieces

Sample beakers, clear glass, 120 mL, suitable for 602041030 OMNIS sample rack, 20 pieces.



FEP tubing / M6 / 150 cm

With light and kink protection



FEP tubing / M6 / 150 cm

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OMNIS

A WHOLE NEW LEVEL OF PERFORMANCE

OMNIS stand-alone license with 2 instrument licenses

Enables stand-alone operation of the OMNIS Software on a WindowsTM computer.

Features:

- The license already includes two OMNIS instrument licenses.
- Must be activated via the Metrohm licensing portal.



907 Titrando

High-end titrator for potentiometric and volumetric Karl Fischer titration with one measuring interface and Dosino dosing units.

- up to four dosing device systems of the 800 Dosino type
- dynamic (DET), monotonic (MET) and endpoint titration (SET), enzymatic and pH-STAT titrations (STAT), Karl Fischer titration (KFT)
- Measurement with ion-selective electrodes (MEAS CONC)
- "iTrode" intelligent electrodes
- Dosing functions with monitoring, liquid handling
- four MSB connectors for additional stirrers or dosing device systems
- USB connector
- For use with OMNIS Software, *tiamo* software, or Touch Control
- Complies with GMP/GLP and FDA regulations such as 21 CFR Part 11, if required



800 Dosino (cable: 1.5 m)

The 800 Dosino is a drive with write/read hardware for intelligent dosing units. With permanently attached cable (length 1.5 m).



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807 Dosing Unit 20 mL

807 Dosing Unit with integrated data chip with 20 mL glass cylinder and light protection, mountable to a reagent bottle with ISO/DIN GL 45 glass thread. FEP tubing connection, antidiffusion tip.



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Electrode Cable 2 m / F

For connecting electrodes with Metrohm plug-in head G to Metrohm instruments (socket F).



Ecotrode Plus

Combined pH electrode for aqueous acid/base titration. The fixed ground-joint diaphragm is insensitive to contamination. Reference electrolyte: c(KCl) = 3 mol/L, storage in storage solution.



Lid tray for OMNIS Sample Robot S

Lid tray for assembly on OMNIS pump module or 6.02007.000 dummy panel attachment in the OMNIS Sample Robot S system.



Dis-Cover lid for OMNIS 120 mL sample beaker, 16 pieces

Dis-Cover lid for 120 mL 6.01400.200, 6.01400.300 and 6.01400.303 sample beakers in the OMNIS Sample Robot Pick&Place system.



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