Application Note AN-T-218

Analysis of Li-ion battery cathode materials made from Co, Ni, and Mn

Fully automated determination including sample preparation using the OMNIS pipetting equipment

The lithium-ion battery market is continuously growing due to the tremendous demand for items like handheld electronics, electric vehicles, and other battery powered consumer products. The quality of these batteries improves continuously by modifying and improving the main components (e.g., cathode, anode, slurry, and separators).

So-called «NCMs», a mixture of nickel, cobalt, and manganese oxides, have been gathering interest as cathode materials. These materials replace the cobalt oxides traditionally used in Li-ion batteries. Quality analysis of the post-sintered materials or recycled batteries can be performed by titration, as demonstrated in this Application Note. A fully automated analysis of the corresponding metals can be performed with OMNIS and its pipetting equipment. For this purpose, only small sample amounts are needed which are accurately transferred to titration beakers for analysis.

SAMPLE AND SAMPLE PREPARATION

The method is demonstrated using dissolved mixtures of Ni, Co, and Mn ion standards.

EXPERIMENTAL

For the metal determination, three titrations are performed. In the first titration, the total metal content is determined with a complexometric titration in an alkaline buffered solution using an excess of EDTA as a ligand for the metal ions, and copper(II) sulfate as a titrant. A Cu ISE was used as a potentiometric sensor. Nickel and cobalt can be determined with the same complexometric titration, but in slightly acidic environments.

The determination of Mn and Co is performed in alkaline conditions with a combined Pt ring electrode and potassium hexacyanoferrate ($K_3[Fe(CN)_6]$) as the titrant. With these determinations the individual metal content of Ni, Co, and Mn can be calculated.
While it is possible to work on two Pick&Place modules, the sample throughput can be increased if a system with three Pick&Place modules is used.

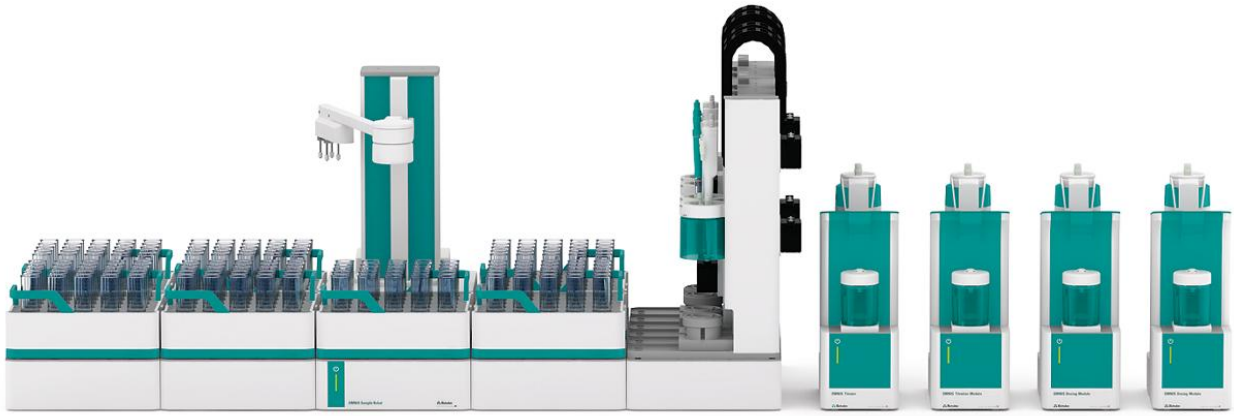

Figure 1. Exemplary OMNIS system for the fully automatic determination of NCMs in lithium-ion battery cathode materials.

RESULTS

The analysis demonstrates acceptable results and well-defined titration curves. The results and an example titration curve are displayed in Table 1 and Figure 2, respectively.

Table 1. Determined metal content of Ni, Co, and Mn in Li-ion battery cathode materials.

Analyte	Recovery in %	SD(rel) in %
Ni	100.66	0.38
Co	101.56	1.10
Mn	97.68	2.29

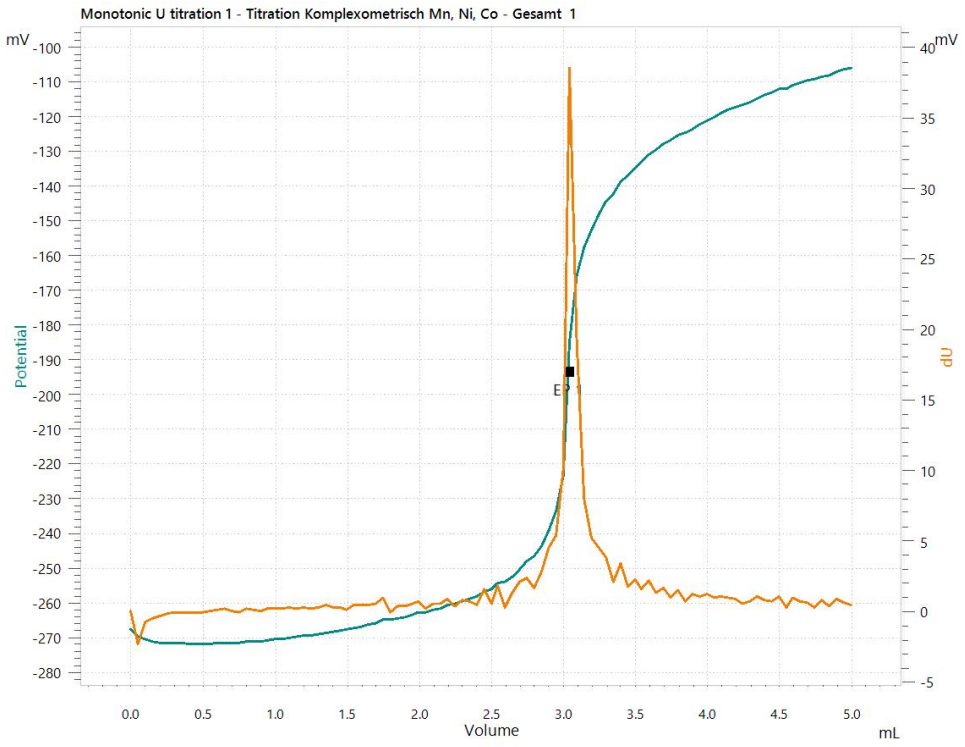

Figure 2. Example titration curve for the total metal content in cathode materials determined by complexometry.

CONCLUSION

With the OMNIS automated pipetting system, NCMs can be determined both quickly and accurately with little sample consumption (< 1 mL). The method is accurate and can not only be used for single elements, but also for sample mixtures consisting of nickel, cobalt, and manganese.

Internal reference: AW TI-CH1-1313-082020

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CONFIGURATION

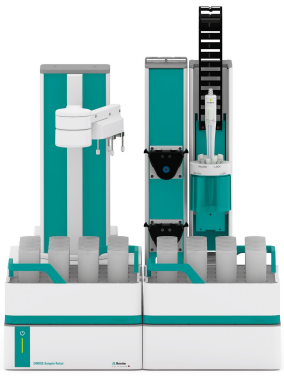
OMNIS Professional Titrator with magnetic stirrer

Innovative, modular potentiometric OMNIS Titrator for stand-alone operation or as the core of an OMNIS titration system for endpoint titration and equivalence point titration (monotonic/dynamic). Thanks to 3S Liquid Adapter technology, handling chemicals is more secure than ever before. The titrator can be freely configured with measuring modules and cylinder units and can have a rod stirrer added as needed. Including "Professional" function license for parallel titration with additional titration or dosing modules.

- Control via PC or local network
- Connection option for up to four additional titration or dosing modules for additional applications or auxiliary solutions
- Connection option for one rod stirrer
- Various cylinder sizes available: 5, 10, 20 or 50 mL
- Liquid Adapter with 3S technology: Secure handling of chemicals, automatic transfer of the original reagent data from the manufacturer

Measuring modes and software options:

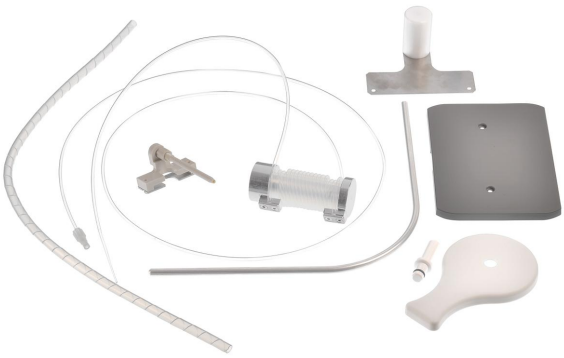
- Endpoint titration: "Basic" function license
- Endpoint and equivalence point titration (monotonic/dynamic): "Advanced" function license
- Endpoint and equivalence point titration (monotonic/dynamic) with parallel titration: "Professional" function license



OMNIS Sample Robot S Pick and Place

OMNIS Sample Robot S with a "Peristaltic" (2-channel) pump module and a Pick&Place module in addition to extensive accessories for the direct transition to fully automatic titration. The system provides space in two sample racks for 32 sample beakers of 120 mL each. This modular system is supplied completely installed and can thus be put into operation in a very short time.

The system can also be extended upon request to include two additional peristaltic pumps and another Pick&Place module, thus doubling the throughput. If additional workstations are required, then this Sample Robot is already able to be expanded to become an L-sized OMNIS Sample Robot, thus enabling samples from seven racks to be processed in parallel on up to four Pick&Place modules and quadrupling the sample throughput.



OMNIS pipetting equipment

Complete accessory set for converting the OMNIS Sample Robot Pick&Place into a version with pipetting options. The set can be mounted on all versions of the OMNIS Sample Robot (S,M and L).

Ion-selective electrode, Cu

Copper-selective electrode with crystal membrane.
This ISE has to be used in combination with a reference electrode and is suitable for:

- ion measurements of Cu2+ (10-8 to 0.1 mol/L)
- ion measurements in small sample volumes (minimum immersion depth 1 mm)
- Complexometric titrations with CuEDTA

Thanks to the robust/break-proof plastic shaft made of EP, this sensor is mechanically very resistant.
The polishing set supplied enables easy cleaning and renewing of the electrode surface.

Combined Pt ring electrode

Combined platinum ring electrode with a ceramic pin diaphragm.

This electrode is well suited for redox titrations when the pH value varies, e.g.:

- oxygen content according to Winkler
- determination of hydrogen peroxide with $KMnO_4$
- diazotization titrations

c(KCl) = 3 mol/L is used as reference electrolyte and storage solution.