

# Laboratory Products

## Battery cells love it dry – how to measure the moisture in the materials

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### 1. Introduction.

Electromobility is a declared goal both to solve resource problems in fuel production and to reduce environmental pollution.

Battery development, which has made great strides in recent years in particular, is seen as the key to progress in electromobility. A lot has happened since 1981 when the Golf I CitySTROMer from Volkswagen drove a maximum of 60 km with lead-gel batteries and the trunk and other space reserves were completely filled with 16 lead-acid batteries [1].

The development towards hybrid and pure electric technology in the automotive industry depends to a large extent on the performance and the costs of the electricity storage media. High energy densities of up to 150 Wh/kg and long cycle lives of >2000 charging cycles are prerequisites for acceptable ranges in motor vehicle use.

In addition to the automotive industry, battery developments are also the key to the extensive use of renewable energies. Stationary, decentralised energy storage systems must have a very high energy content, while being low-maintenance and durable.

Lithium-ion batteries are one of the successful developments. They have significant advantages over conventional batteries such as lead-gel, nickel-cadmium and nickel-metal hydride. They have high rated voltages of 3.4-3.7 V, very high current densities, no memory effect, constant discharge voltage, low self-discharge. This results in a high efficiency of 95% and a compact, lightweight design. However, lithium-ion systems require special precautions when charging, cannot be used at temperatures above 60°C, and must be secured with built-in protective electronics (PCB) [2]. This results in a correspondingly high price.

Li-ion batteries for motor vehicles today achieve an energy density of over 120 Wh/kg compared to lead-acid batteries with around 30 Wh/kg. A large number of parameters are responsible for the performance of battery systems. Decisive factors for the energy density and performance of lithium-ion batteries are the choice of materials and the purity of the components used.

For example, over the years, e.g. the capacity of the 18650-type accumulators (design comparable to conventional AAA batteries) from 1991 to 2005 tripled to 2550 mAh by changing the electrode materials and the electrolytes used [3]. Today, the energy densities of this type are even 3500 mAh.

Lithium-ion batteries consist of the following basic components:

- 1. Electrode: e. g.  $\text{LiCoO}_2$
- 2. Electrode: e. g. Li-Graphite
- Electrolyte: water free, e. g. Ethylene carbonate, Dimethyl carbonate, Fluorine ethylene carbonate with conducting salt: e. g.  $\text{LiPF}_6$
- Separator made of porous membranes (polypropylene, polyethylene, ceramic)

The entire structure of the lithium-ion battery must be such that the water content is very low ( $\text{H}_2\text{O}$  content <20 ppm), otherwise the water will react with the conducting salt  $\text{LiPF}_6$  to form HF (hydrofluoric acid). The hydrofluoric acid leads to a strong reduction in capacity and service life. For production and development, this means constant monitoring of the water content in all the basic materials and assemblies used (electrode materials, separator membranes, basic electrolytes, conducting salt, functional passivation additives, additives for cathode and flame retardants [4,5]).

Due to the very low water content, the determination can only be carried out with certainty using a coulometric titration.

Investigation of the solids also requires the use of the heating technique with an oven to release the trapped water.

### 2. Metrology

The coulometric titration is based on the electrochemical generation of the iodine required for the Karl Fischer determination. According to Faraday's law and the

Karl Fischer reaction equation, the amount of water converted can be determined immediately from the amount of electrical charge. The advantage of this coulometric method is that no titre adjustment is required. The titration end point is indicated electrochemically with the aid of two platinum electrodes.

With the coulometric titration, even the smallest amounts of charge can be 'dosed' with high precision. For this reason, the coulometric variant of the Karl Fischer technique has established itself in the trace area.

Liquids are injected into the measuring cell through a septum. This direct dosing can be used if no disturbing side reactions occur. A prerequisite for reliable analyses in the trace range is an intact septum to prevent the ingress of atmospheric moisture. In addition, all-glass cells are advantageous.

Direct dosing is only suitable to a limited extent for solids and liquids that are insoluble in the Karl Fischer reagent. It is better, but more labour intensive, to extract the water beforehand with a suitable solvent (e. g. methanol or dioxane). However, other methods of sample pretreatment (homogenisation, crushing, extraction) increase the risk of measurement errors, especially in the ppm range, due to the influence of the ambient humidity.

The heating technique represents a very elegant and universal alternative for solids, pasty materials and oils, with which the water can be selectively determined.

The sample to be analysed is dosed into a separate oven. At elevated temperatures, the water is heated out of the sample and transported to the coulometric measuring cell with the help of a dried carrier gas stream. For reliable analysis results in the ppm range, the continuously flowing carrier gas must be dried very carefully.

It is more expedient to circulate the carrier gas, as implemented in the AQUA 40.00 Vario from ECH Elektrochemie Halle GmbH (Figure 1).



Figure 1: Karl Fischer titrator with heating technology (AQUA 40.00 Vario Plus).

The heating principle is that the gas in the measuring cell is extracted by a pump and pumped through the heating oven. The gas mixture enriched with the water from the sample is then fed back into the measuring cell (Figure 2).

With this circulation, the gas is practically 'dry titrated' and no separate, time-consuming gas drying is required. Another great advantage is that there is no evaporation of methanol from the Karl Fischer reagent, which would lead to contamination of the laboratory air.

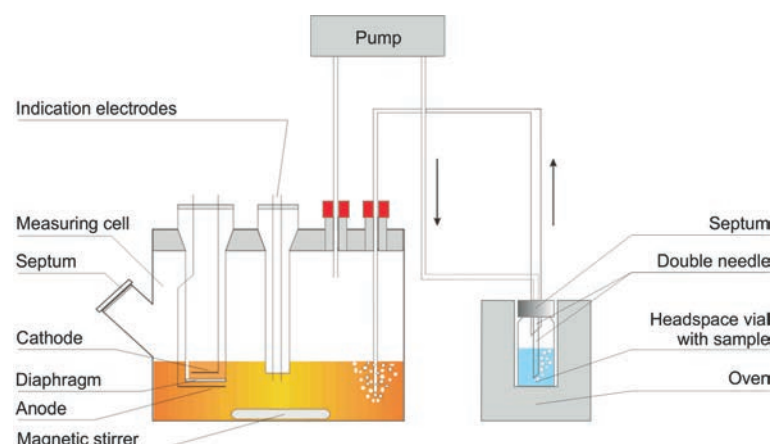


Figure 2: Gas extraction principle with closed loop.

The powdery, granulated, pasty samples or foils are weighed into glass vials with a tight-fitting septum cap. For the measurement, a double-needle system pierces the septum and transports the heated water vapor into the measuring cell.

In addition to working with a constant temperature, the sample can also be heated with a temperature ramp. The heating rate is freely programmable in the range from 0.1 to 10 °K/min. This computer-controlled temperature gradient heating is a quick way to develop optimal heating methods for different sample types. There are interesting starting points for further interpretation of the measurement results. In this way, the Karl Fischer titration represents an instrument for determining substance-specific properties.

In the following, a number of examples will be used to show which peculiarities can occur when determining the water content in battery materials and which methods are suitable.

### 3. Water content determination in electrolytes

Determining the water content in basically anhydrous electrolytes is one of the most demanding tasks. Electrolytes are measured using direct coulometric titration. The use of an oven technique is not recommended because the conducting salts can be thermally unstable.

Careful sampling is the basis for correct measured values. The highly hygroscopic samples absorb water as soon as they are filled into a sample container for transport to the laboratory, especially if the bottles are not filled to the brim and then sealed airtight. If possible, the bottle should not be opened to take an aliquot of the sample; a lid with a septum cap is recommended here. Due to the high volatility and high concentration of conducting salts, drawing it up in the cannula quickly leads to crystallisation. The sample should be withdrawn slightly in the cannula.

In addition, contact with atmospheric moisture leads to the decomposition of the conducting salt and corrosion of the steel cannulas, particularly in the case of mixtures containing  $\text{SO}_2$ . The use of disposable syringes and cannulas has proven itself. Sampling in a dry glove box atmosphere can be recommended.  $\text{SO}_2$ ,  $\text{S}_2$  and sulfonates do not interfere with the titration, mercaptans can be masked with N-ethylmaleimide.

However, some additives falsify the results, e. g. dimethyl sulfoxide gives low results, sulfonyl and thionyl chloride react with water. In the case of sluggish titrations and constantly increasing drifts, Karl-Fischer reagents without alcohol can be used. These are on offer recently e.g. from Honeywell specifically for the battery materials [6].

A typical measurement curve can be seen in Figure 3.

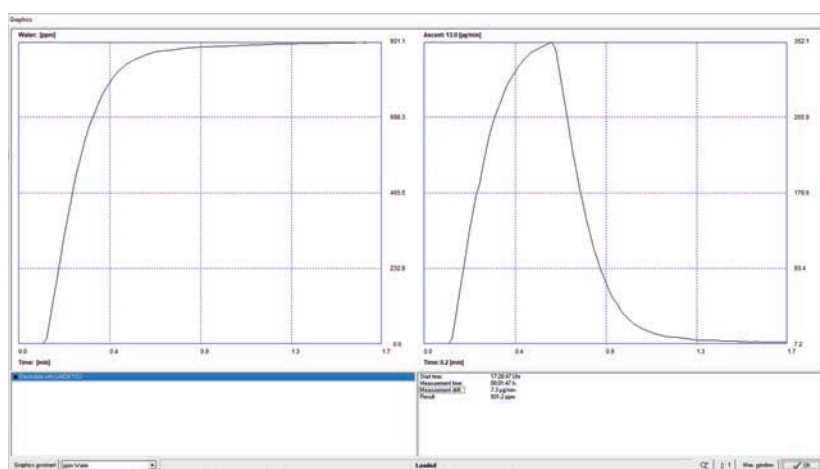


Figure 3: Titration curve of electrolytes with  $\text{LiAlCl}_4 \cdot \text{SO}_2$ .

In our investigations, we found that standard addition using a NIST-traceable liquid standard can be very helpful in verifying the measurement method in your own laboratory.

This standard addition is performed by adding a specified amount of liquid standard (e. g. 1 ml 1000 ppm standard) to a precisely defined volume of the electrolyte sample in a sealed vial with a septum cap. Another vial with the same amount of sample but without standard addition is prepared at the same time.

The standard is dosed using a disposable syringe, and a disposable syringe without filling is also briefly pierced through the second vial. Both vials are shaken briefly. 1 ml of each sample is measured quickly. With this procedure, the difference between the two types can be determined and the correctness of the analysis can be verified based on the recovery of the standard. The moisture in the vials, cannulas and handling steps that occurs during the procedure is also taken into account. The advantage of liquid standard dosing is that the dosed amount can be placed exactly in the range of the sample to be analysed. Because in the coulometric titration, only the absolute titrated amount of water ( $\mu\text{g}$ ) in the titration cell is important; depending on the sample volume, this can reflect different concentrations.

Figure 4 shows the high reproducibility when repeating the measurement of highly hygroscopic battery electrolytes. This can be achieved with careful work and a high density of the titration cell.

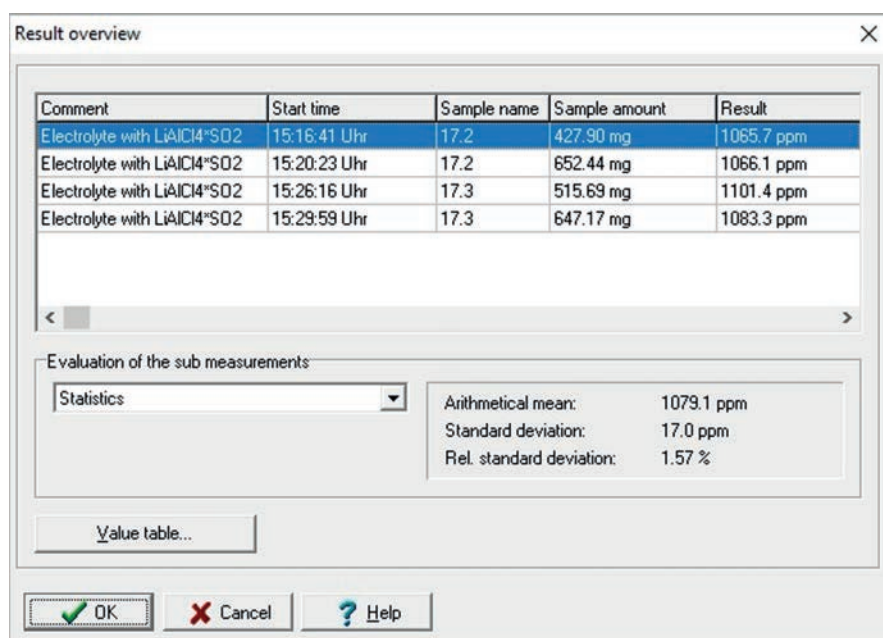


Figure 4: Reproducibility of water determination in electrolytes with  $\text{LiAlCl}_4 \cdot \text{SO}_2$  – one software evaluation.

### 4. Measurements in solid electrode materials

The powdery, granulated, pasty samples or foils are weighed into glass vials with a tight-fitting septum cap. For the measurement, a double-needle system pierces the septum and transports the heated water vapor into the measuring cell.

In addition to working with a constant temperature, the sample can also be heated with a temperature ramp. The heating rate is freely programmable in the range from 0.1 to 10 °K/min. This computer-controlled temperature gradient heating is a quick way to develop optimal heating methods for different sample types. There are interesting starting points for further interpretation of the measurement results.

Figure 5 shows an example of temperature-controlled heating of the moisture from carboxymethyl cellulose. The curve can be used to determine the optimal heating temperature (here 150 °C) at which the water can be separated from the solid sample very quickly without the sample thermally decomposing.

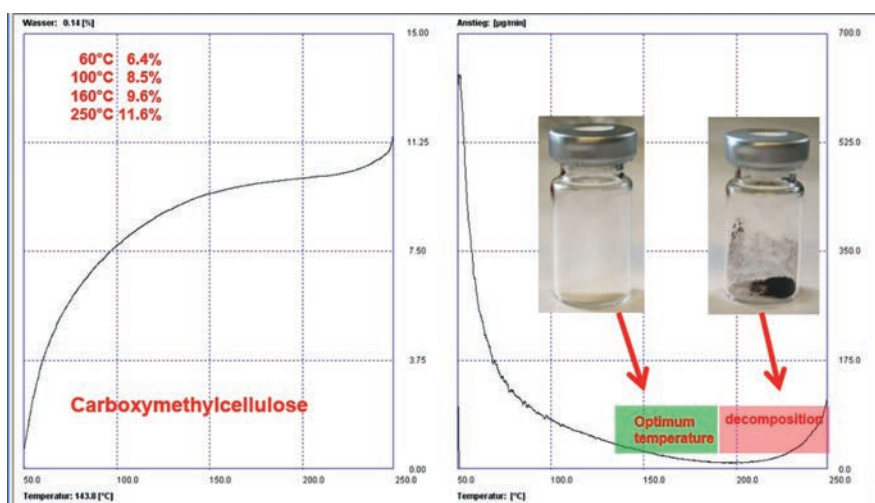


Figure 5: Water release from carboxymethyl cellulose as a function of temperature (temperature program 50-250 °C, 3K/min).



The analysis of the various solid or pasty components of the batteries can be carried out very reproducibly, since no sample preparation steps are usually necessary for the introduction of the sample into the heating oven. Various vial sizes are available, which also allow larger components, preforms or pieces of membrane to be positioned in the vial without crushing or grinding. Any kind of sample pre-treatment would bring moisture from the room air to the surface of the sample.

Figure 6 shows examples of different sizes of sample containers. Different inserts and sample trays are available for each vial size. The adjustments to the headspace oven and the autosampler can be carried out very easily by the user. It should be noted that the larger the sample container, the more humidity it contains, so that the blank value of the container also increases.



Figure 6: Different sample containers for different sample types.

Table 1 shows measurements for different electrode materials. They show the high reproducibility of the analysis, although different weights were used. The samples are partly piece plates of electrode faces. Nevertheless, the measurement time is very short at 10-20 minutes.

Table 1: Reproducibility of measurements of the water content for powdered electrode material (100°C) using headspace technology.

Meas. -No.	Sample name	Sample amount [mg]	result - absolute [ $\mu\text{g}$ ]	Result [%]
1	Li-Ni-CO-Mn-Oxide	221.07	223.5	0.10
2		153.80	149.8	0.10
3		220.80	216.6	0.10
		Mean value		0.10%
		Rel. Standard deviation		2.00%
4	Li-Fe-Phosphate	132.15	532.2	0.40
5		178.50	734.6	0.41
6		246.45	1008.6	0.41
		Mean value		0.41%
	Rel. Standard deviation		1.12%	

The aim of battery manufacture is to use all components with as little water as possible so that the water content in the finished product is as low as possible and storage up to 60°C does not lead to water release. Accordingly, the materials are intensively pre-dried. The resulting water content not only depends on the conditions of the process dryer, but in particular on the subsequent processes, as can be seen in the following example.

A high-temperature furnace capable of heating samples up to a temperature of 1300°C (Figure 7) was used for the analyses.  $\text{LiCoO}_2$  and graphite require high temperatures for complete release of the trapped water. The water released from the samples is transported into the titrator with the aid of a pre-dried stream of argon or nitrogen. The samples are weighed into ceramic sample boats. This means that up to 5 g of sample can be used. The determination is blank-free.



Figure 7: High-temperature oven coupled with coulometric Karl Fischer titration.

Figure 8 shows a series of tests to determine the water content in freshly dried  $\text{LiCoO}_2$  powder. The powder was dried at 600°C.

The periods of time between sampling and measurement have been varied. Just three minutes of exposure to air increases the water content threefold again. Such investigations show the great importance of the procedure both in the production process and in the sampling for the analysis of such materials.

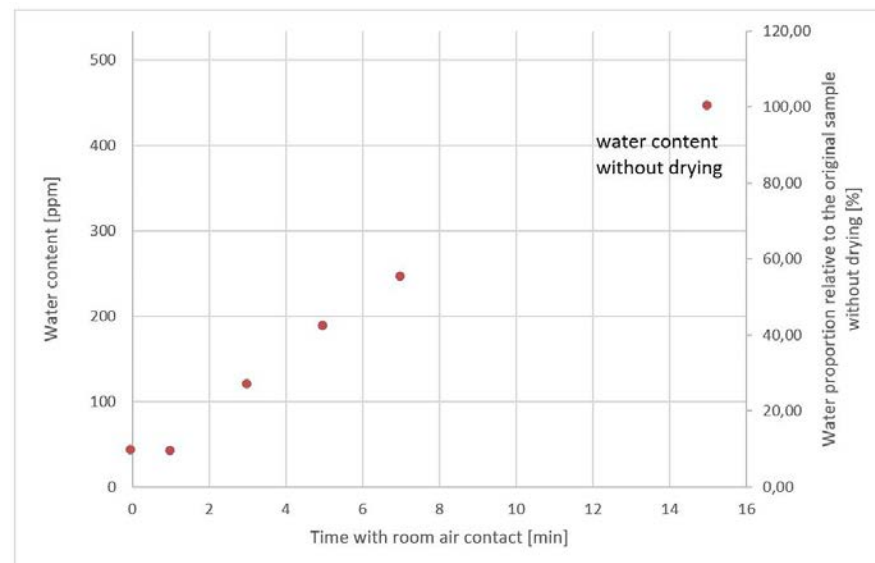


Figure 8: Measurements of the water content of powdered electrode material ( $\text{LiCoO}_2$ ) after removal from the drying process (20 min, 600°C).

Glove boxes are used to avoid any falsifying influence of humidity on the battery materials. In these miniature rooms, the atmosphere can be pre-dried in a controlled manner and made oxygen-free. The example shown in Figure 9 is precisely adapted to the measurement task. An analytical balance and the Karl Fischer titrator with headspace technology are positioned in the closed room. The processes inside can be carried out from the outside using up to four glove box gloves. An airlock on the side of the glove box is used for loading and unloading the materials. With this technique, the blank value in the analyses is reduced to < 10  $\mu\text{g}$ , so that highly sensitive trace analyses in the battery materials are possible.



Figure 9: Arrangement of the Karl Fischer titrator and the analytical balance in a customised glove box with four glove ports

## 5. Summary

The coulometric Karl Fischer titration is the most suitable method for investigating the water content of battery materials. By coupling a heating technique with sealed sample vials, the highly hygroscopic materials can also be analysed successfully. The variation of the heating parameters enables the water content to be determined in the entire range of the electrode, electrolyte and foil materials used. The procedure for representative sampling is the key to accurate and correct analyses for process monitoring.

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