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TECHNICAL SPECIFICATION

colour
inside

Nanomanufacturing – Key control characteristics –
Part 4-8: Nano-enabled electrical energy storage – Determination of water content in electrode nanomaterials, Karl Fischer method

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CONTENTS

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NANOMANUFACTURING –
KEY CONTROL CHARACTERISTICS –

Part 4-8: Nano-enabled electrical energy storage – Determination of water content in electrode nanomaterials, Karl Fischer method

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Technical Specifications are subject to review within three years of publication to decide whether they can be transformed into International Standards.

IEC TS 62607-4-8, which is a Technical Specification, has been prepared by IEC technical committee 113: Nanotechnology for electrotechnical products and systems.

The text of this Technical Specification is based on the following documents:

DTS	Report on voting
113/491/DTS	113/515/RVDTS

Full information on the voting for the approval of this Technical Specification can be found in the report on voting indicated in the above table.

This document has been drafted in accordance with the ISO/IEC Directives, Part 2.

A list of all parts in the IEC 62607 series, published under the general title *Nanomanufacturing – Key control characteristics*, can be found on the IEC website.

The committee has decided that the contents of this publication will remain unchanged until the stability date indicated on the IEC website under "http://webstore.iec.ch" in the data related to the specific publication. At this date, the publication will be

- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

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INTRODUCTION

Nano-enabled electrical energy storage has been applied in many fields such as portable electronics, electric vehicles and energy storage systems. With continuous rapid development in these applications, nano-enabled electrical energy storage with high performance is in demand. The main properties of the electrical energy storage device are determined by its electrode nanomaterials.

The water content for electrode nanomaterials is one of the important characteristics to be determined as a quality control test. Water can affect electrical performance, cycling performance and safety performance of nano-enabled electrical energy storage devices [1][1], [2]. A high amount of water from electrode materials has a critical influence on both active materials and battery cells [3], and might affect performance or safety characteristics.

Several methods are available for the determination of water content. Karl Fischer titration method is a direct method that is suitable for testing water in gas, liquid and solid samples. The method is useful for low water content levels (< 1 %). Especially, Karl Fischer coulometric titration method is an absolute method which can determine the water content from the quantity of electricity consumed during the test. It can detect trace levels of free water (ppm level), which cannot be detected with normal drying or gravimetric methods. The Karl Fischer coulometric titration method is capable of distinguishing water levels as low as 0,0001 %.

At present, there are 21 International Standards and/or Technical Specifications mentioning the Karl Fischer method to measure water content, of which 16 use the volumetric titration method, and 5 use the coulometric titration method. The accuracy and resolution of the volumetric method is not appropriate for electrode nanomaterials, whose water content is lower than 1 %. The sampling and measurement controls of the current coulometric method standards are not appropriate for electrode nanomaterials, which have highly hygroscopic characteristics. Therefore, the present standards are not suitable for electrode nanomaterials. This document, considering a sample's characteristic, will help to determine the water content of the electrode nanomaterials in a short time with high accuracy, and will be helpful for quality control in laboratories and industrial manufacturers.

This standardized method is intended for use in comparing the characteristics of raw materials [e.g. lithium cobalt oxide (LCO), lithium nickel cobalt aluminium oxide (NCA), lithium nickel cobalt manganese oxide (NCM), and lithium iron phosphate (LFP)] without any additives [e.g. carbon nanomaterials like carbon black (CB), carbon nanotubes or fibres] or organic binder [e.g. polyvinylidene difluoride (PVDF) or styrene-butadiene rubber (SBR)], their selection process and as a quality control method for the fully formulated electrode material, not for evaluating the electrode in end products.

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[1] Numbers in square brackets refer to the Bibliography.

NANOMANUFACTURING –
KEY CONTROL CHARACTERISTICS –

Part 4-8: Nano-enabled electrical energy storage – Determination of water content in electrode nanomaterials, Karl Fischer method

1 Scope

This part of IEC 62607, which is a Technical Specification, specifies a test method for the determination of water content in electrode nanomaterials for nano-enabled electrical energy storage devices, using the Karl Fischer coulometric titration method.

This document includes:

- recommendations for sample preparation,
- outlines of the experimental procedures used to measure electrode nanomaterial properties, and
- methods of interpretation of results and discussion of data analysis.

NOTE This method has precision as low as 0,000 1 %. The best applicable measure range is 0,01 % to 1 %.

This document is not applicable for samples that can react with the main components of Karl Fischer reagent and produce water, or samples that can react with iodine or iodide ion.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 760, *Determination of water – Karl Fischer method (General method)*

ISO 12492, *Rubber, raw – Determination of water content by Karl Fischer method*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

3.1
nanoscale
length range approximately from 1 nm to 100 nm

Note 1 to entry: Properties that are not extrapolations from larger sizes are predominantly exhibited in this length range.

[SOURCE: ISO/TS 80004-1:2015 [4], 2.1]

3.2

nanomaterial

material with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale

Note 1 to entry: This generic term is inclusive of nano-object and nanostructured material.

[SOURCE: ISO/TS 80004-1:2015 [4], 2.4]

3.3

electrode nanomaterial

material used in nano-enabled energy storage devices such as lithium-ion batteries or electrochemical capacitors which contains a fraction of nanomaterial and exhibits function or performance made possible only with the application of nanotechnology

Note 1 to entry: In this document, it refers to the raw material powders (e.g. LCO, NCA, NCM, and LFP) without any additives (e.g. carbon nanomaterials like CB, carbon nanotubes or fibres) or organic binder (e.g. PVDF or SBR).

[SOURCE: IEC TS 62607-4-3:2015 [5], 3.1.1]

3.4

water content

percentage mass fraction of water as determined in accordance with the method specified in this document

[SOURCE: ISO 8534:2017 [6], 3.1, modified – In the definition, "mass, in grams per 100 g of sample," has been replaced by "percentage mass fraction".]

3.5

dew-point

temperature at which the vapour pressure of the vapour in a humid gas is equal to the saturation vapour pressure over the pure liquid and at which condensate forms as a liquid on cooling the gas

[SOURCE: ISO 7183:2007 [7], 3.7]

4 Principle

In the Karl Fischer method, water (H_2O) reacts quantitatively with iodine (I_2) and sulfur dioxide (SO_2) in the presence of a lower alcohol such as methanol (CH_3OH)) and an organic base (RN) to produce iodide ion, as follows:

$$H_2O + I_2 + SO_2 + 3RN \rightarrow 2(RN{+}H)I^- + RN{\cdot}SO_3 \tag{1}$$

$$RN{\cdot}SO_3 + CH_3OH \rightarrow (RN{+}H){\cdot}SO_4{\cdot}CH_3 \tag{2}$$

where

RN is an organic base.

In coulometric Karl Fischer titration, iodine (I_2) is generated electrochemically from iodide (I^-). When iodine (I_2) comes in contact with the water in the sample, water is titrated according to the reaction (1) and (2). Once all of the water available has reacted, the reaction is complete. The amount of water in the sample is calculated by measuring the current needed for the electrochemical generation of iodine (I_2) from iodide (I^-) according to the following reaction:

$$2I^- \rightarrow I_2 + 2e^- \tag{3}$$

According to Faraday's Law of electrolysis Equation (4), the quantity of the iodine produced is proportional to the current generated. Iodine and water react with each other in proportion of 1:1 stoichiometrically, as shown in reaction (1). Therefore, 1 mole of water (18 g) is equivalent to 2 × 96 500 C, or 10 722 C per 1 g of H_2O. Based on this principle, it is possible to determine the amount of water from the quantity of electricity consumed, according to Equation (5):

$$m = KQ \tag{4}$$

$$m = \frac{18}{2 \times 96500} \times Q = \frac{1}{10722} \times Q \tag{5}$$

where

m is the mass of water, g;

K is a proportional constant (electrochemical equivalent);

Q is the quantity of electricity, C.

5 Reagents

Use only reagents of recognized analytical quality, and distilled or demineralized water or water of equivalent purity.

5.1 Coulometric Karl Fischer reagent

Standard, commercially available coulometric Karl Fischer reagents as described in ISO 760.

5.2 Methanol (anhydrous)

Methanol (anhydrous) with minimum purity with a mass fraction of 99,9 % and maximum water content with a mass fraction of 0,1 % (preferably less than 0,05 %).

5.3 Carrier gas

Instrument grade of dry carrier gas (e.g. nitrogen gas), at least with a volume fraction of 99,999 %, should be used in all tests.

5.4 Water standard for Karl Fischer coulometric titration

Standard, commercially available water standard with a mass fraction of 0,1 %.

6 Apparatus

6.1 Karl Fischer coulometric titration apparatus

Karl Fischer apparatus should contain titration cell, platinum electrodes, magnetic stirrer, and control unit. Example of Karl Fischer coulometric titration apparatus is shown in Figure 1.

6.2 Evaporator

The water evaporator should contain a drying oven capable of heating the test portion to 300 °C, a temperature control unit, a carrier gas flow meter and carrier gas drying tube (water absorption tube) containing desiccant. Example of evaporator is shown in Figure 1.