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TECHNICAL SPECIFICATION

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Nanomanufacturing – Key control characteristics –
Part 6-13: Graphene-based material – Oxygen functional group content: Boehm titration method

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FOREWORD

The main task of IEC technical committees is to prepare International Standards. In exceptional circumstances, a technical committee may propose the publication of a Technical Specification when

- the required support cannot be obtained for the publication of an International Standard, despite repeated efforts, or
- the subject is still under technical development or where, for any other reason, there is the future but no immediate possibility of an agreement on an International Standard.

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

IEC TS 62607-6-13, 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:

Draft TS	Report on voting
113/455/DTS	113/486/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 of 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 document will remain unchanged until the stability date indicated on the IEC website under "http://webstore.iec.ch" in the data related to the specific document. At this date, the document will be

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- withdrawn,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

The contents of the corrigendum of October 2020 have been included in this copy.

IMPORTANT – The 'colour inside' logo on the cover page of this publication indicates that it contains colours which are considered to be useful for the correct understanding of its contents. Users should therefore print this document using a colour printer.

INTRODUCTION

In recent years, graphene has attracted extensive attention from academia and industry, due to the extraordinary physical and chemical properties for promising applications in energy conversion and storage, electronics, composites and catalysis, etc. In the case of most graphene available in the laboratory or on the market, oxygen functional groups are inevitable, especially for the powder form products. These oxygen functionalities, which exist mainly in the form of carboxyl groups, lactones or lactols, phenolic hydroxyl groups, reactive carbonyl groups and epoxide groups, etc., are located on the surface or edge of the two-dimensional carbon lattice. They affect many crucial properties of graphene, including wettability, electrical and thermal conductivity, electron density, acidity and reactivity, etc. [1][2][3][4][1], and so determine the performance of graphene for downstream applications. For example, in an energy storage device such as lithium ion battery or supercapacitor, the oxygen heteroatoms will introduce irreversible reaction to exhaust the organic electrolyte and emit small molecules, which will reduce the cycling stability and even cause safety problems to the final products [5][6]. Besides, the oxygen functional groups will significantly decrease the electrical conductivity of graphene, which has a negative impact on the rate capacity of the cell, due to the increase of internal resistance for the electrode [7][8]. Furthermore, the different oxygen containing functional groups will play very different roles in affecting the properties of graphene. For example, in catalysis, graphene has been employed as an effective solid acid catalyst for hydrocarbon chemistry, as many oxygen functionalities show acidic properties [9][10][11]. However, the acidity strength of different oxygen species is distinct, as the acidity sequence is carboxyl, lactone, hydroxyl, and carbonyl. Besides, it is proved that ketonic carbonyl groups, with higher electron density, are the catalytic active sites for oxidative dehydrogenation reactions [12][13]. So, the type and proportion of oxygen groups will significantly influence the catalytic activity and selectivity of graphene. Therefore, the qualification of different oxygen functional groups on the surface of graphene is a key control characteristic for the production, application and trading of graphene and related products.

The most common methods for identification and quantification of oxygen functional groups on graphene are FT-IR, XPS, EELS and Boehm titration. Moreover, other recent methods such as SAED, MS and FLOSS are springing up. However, some of these methods have difficulty quantifying oxygen functional groups on graphene, and there is no standard method to quantify the oxygen functional groups. Boehm titration, dating from 1962, is an efficient, repeatable and easy to operate method with low cost. More importantly, the Boehm titration method can provide absolute values of the surface concentration of oxygen functional groups and avoid the ambiguity and subjectivity brought by spectroscopies, which shows its unique advantage in quantification of many oxygen functional groups on graphene [14][15][16][17][18][19][20]. Note that Boehm titration cannot determine the total oxygen content of a powder, as it only measures those functional groups that can dissociate under the conditions of the test.

Boehm titration has been applied to determine the oxygen functional groups of many traditional carbonaceous materials for decades, such as activated carbon and carbon black. In recent years, it was applied to graphene [21][22]. Because the physical properties of graphene are very different from those of other carbonaceous materials, the operation-specific details in this document are suitable for powders of graphene oxide, reduced graphene oxide, graphene and related materials only. When applying Boehm titration to graphene dispersions, the dispersion medium needs to be removed. This document can be used as the reference for other carbonaceous materials.

This document focuses on the determination of oxygen functional groups and standardization of the operation method. Due to various steps such as agitation, end-point determination, etc. required in Boehm titration, significant measurement errors can be introduced if not properly addressed.

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

NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

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1 Scope

This part of IEC TS 62607 establishes a standardized method to determine the chemical key control characteristic

- oxygen functional group content

  for powder consisting of graphene-based material like graphite oxide, graphene oxide, reduced graphene oxide and other types of functionalized graphene by

- Boehm titration method.

In this document, the measured functional groups are carboxyl groups (also in the form of their cyclic anhydrides), lactone groups, hydroxyl groups and reactive carbonyl groups. Oxygen functional groups that exhibit no reactivity such as epoxides cannot be measured.

The oxygen functional group content is derived by the difference between $NaHCO_3$, Na_2CO_3, NaOH and C_2H_5ONa consumption of dispersed graphene powders.

– The oxygen functional group content determined according to this document is listed as key control characteristic in the blank detail specification for graphene IEC 62565-3-1.

– The method is applicable for graphene powder and graphene related carbon 2D materials such as graphene oxide powder and reduced graphene oxide powder, which can be separated from the water and ethanol by centrifugation or filtration. This document is not applicable for sulfonate modified graphene.

– In this document, the lower limits of detection (Annex C) for carboxyl groups, lactone groups, hydroxyl and carbonyl are 0,015 mmol/g, 0,037 mmol/g, 0,014 mmol/g, and 0,072 mmol/g, respectively.

– This document targets graphene manufacturers and downstream users to guide their material design, production and quality control.

2 Normative references

There are no normative references in this document.