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Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for total electrical conductivity of conductive fine ceramics

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Contents

Page

Foreword .... **iv**
1 Scope **1**
2 Normative references **1**
3 Terms and definitions **1**
4 Symbols **2**
5 Principle **3**
6 Apparatus **3**
6.1 Measurement system 3
6.2 Furnace 3
6.3 Voltmeter 3
6.4 Constant direct current (DC) supply 4
6.5 Wire electrodes and lead wires 4
6.6 Caliper 4
6.7 Micrometer 4
7 Test piece **4**
7.1 Shape and dimensions 4
7.2 Surface roughness 4
7.3 Density 4
7.4 Configuration of four wire electrodes 5
7.5 Number of test pieces 5
8 Test procedure **5**
8.1 Dimension measurement of a test piece 5
8.2 Heating of a test piece 5
8.3 Maintenance of gas composition and gas flow rate 6
8.4 Measurement of total electrical conductivity 6
9 Calculation of total electrical conductivity **6**
10 Expression of total electrical conductivity **7**
10.1 The value of total electrical conductivity 7
10.2 The expression of total electrical conductivity 7
11 Analysis of precision and uncertainty **7**
12 Test report **7**
Bibliography **8**

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 206, *Fine ceramics*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for total electrical conductivity of conductive fine ceramics

1 Scope

This document specifies the test method for the determination of total electrical conductivity of conductive fine ceramics by the DC (direct current) four-terminal method. The test method applies to conductive fine ceramics which have an ionic transference number of 0,01 or less. The applicable conductivity range is from 1 S cm^{-1} to 1 000 S cm^{-1} and the temperature range is up to 1 000 °C. The values expressed in the test method are in accordance with the International System of Units (SI).

This document is intended for industrial product quality control and material development of conductive fine ceramics used in electrodes, e.g. fuel cells, batteries and water electrolysis.

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 3599, *Vernier callipers reading to 0,1 and 0,05 mm*

ISO 3611, *Geometrical product specifications (GPS) — Dimensional measuring equipment: Micrometers for external measurements — Design and metrological characteristics*

ISO 6906, *Vernier callipers reading to 0,02 mm*

ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

ISO 18754, *Fine ceramics (advanced ceramics, advanced technical ceramics) — Determination of density and apparent porosity*

ISO 80000-1, *Quantities and units — Part 1: General*

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:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
total electrical conductivity
electrical conduction where both electrons and ions carry the electrical charges

3.2
electronic conduction
electrical conduction where electrons (or holes) carry the electrical charges

3.3
conductive fine ceramic
substance whose electrical conduction is primarily governed by *electronic conduction* (3.2) rather than ionic conduction

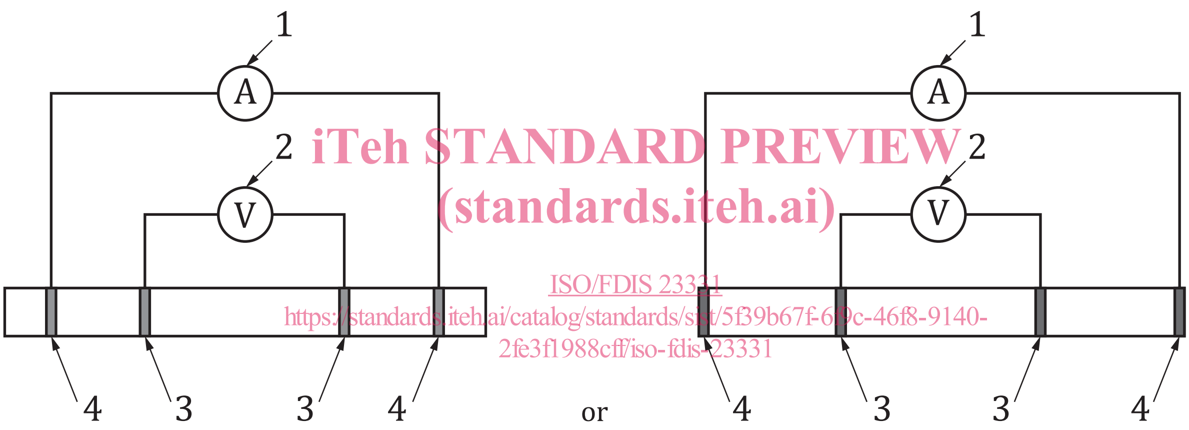
Note 1 to entry: In this document the term indicates a fine ceramic with an ionic transference number of 0,01 or less.

Note 2 to entry: If the ionic transference number is unknown, it shall be confirmed to be smaller than 0,01 using a proper method such as the potentiostatic polarization method, the galvanostatic polarization method or the electromotive force (EMF) method at a temperature range, prior to the measurements.

3.4
DC four-terminal method
method for measuring *total electrical conductivity* (3.1) using direct current (DC) with four terminals

Note 1 to entry: See Figure 1.

Note 2 to entry: Other electrode configurations are acceptable as well. Four wire electrodes are wrapped on a surface of the test piece. The two outer electrodes, called current terminals, supply DC to the test piece. The two inner electrodes, called voltage terminals, measure the voltage. Total electrical conductivity can be determined with the applied current, the measured voltage and the geometry of the test piece.



Key

1 DC supply
2 voltmeter
3 voltage terminal
4 current terminal

Figure 1 — DC four-terminal method

4 Symbols

Symbol	Designation	Unit
σ	Total conductivity	S cm^{-1}
L	Distance between voltage terminals	cm
R	Effective resistance	Ω
A	Cross-sectional area of the test piece	cm^2

5 Principle

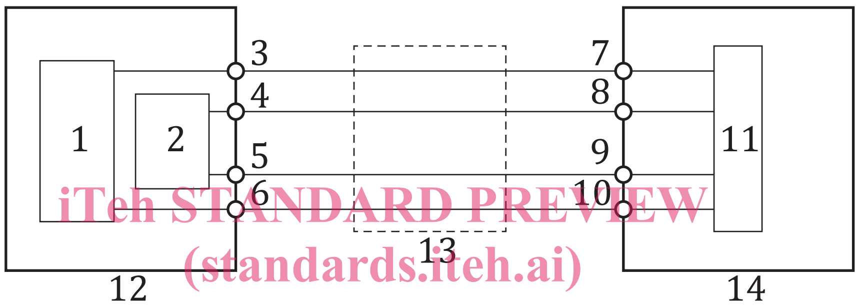
Four wire electrodes are wrapped on the surface of the test piece to be measured. Current is passed through the two outer electrodes and the floating potential is measured across the inner pair. When an external electric field is present, electrons in the valence band can move to the conduction band freely, therefore it is responsible for the electrical conductivity of conductive fine ceramics.

6 Apparatus

6.1 Measurement system

The measurement system shall be composed of a furnace in which a test piece is placed, a voltmeter and four wire electrodes, as shown in Figure 2.

Calibration on a regular basis shall be conducted in accordance with the procedures and methods in the manual provided by the manufacturer or proper reference material, such as electrolytic iron (NIST RM 8420).



Key

1 DC supply
2 voltmeter
3 Hc (current terminal)
4 Hp (voltage terminal)
5 Lp (voltage terminal)
6 Lc (current terminal)
7 hc (current terminal)
8 hp (voltage terminal)
9 lp (voltage terminal)
10 lc (current terminal)
11 test piece
12 measurement unit
13 lead wires
14 furnace

Figure 2 — Measurement system

6.2 Furnace

The furnace should have a hot zone large enough to accommodate the required size of test piece, and be capable of maintaining the test temperature (T) so that the maximum temperature variation in the hot zone is 10 °C. The furnace shall allow a constant heating rate, which can be controlled to within 2 °C/h. The furnace heating elements, thermal insulation and kiln furniture shall be selected to be chemically compatible with the test pieces, avoiding both surface reaction and generation of vapour pressure. The measurements shall be under a gas-flowing condition to maintain a separate gas atmosphere from the ambient atmosphere using a gas-tight furnace tube or combustion tube. If carbide or nitride ceramics are used as a test piece, a protective atmosphere during the experiment should be maintained using noble gas.

6.3 Voltmeter

The voltage measurement of Hp and Lp shall be guaranteed for the operation within the range of measured voltage.

Some voltmeters limit their working voltages of Hp and Lp to protect and stabilize the circuits. If the voltages of Hp and Lp become too high, a large error will appear in these meters. The instrument should have a function for correcting the effects of the lead wires.

6.4 Constant direct current (DC) supply

Constant DC supply shall be possible with a precision of at least three significant digits in the current range of measurement.

The instrument should have a function for correcting the effects of the lead wires.

6.5 Wire electrodes and lead wires

Noble metal, such as platinum (Pt), gold (Au) and silver (Ag), can be used as wire electrodes that should be selected by considering the chemical reaction with the test piece. The lead wires, which connect between the measurement unit and the wire electrodes on the test piece, should be as short in length as possible to avoid influence from external noise and floating capacity. Coaxially shielded cables should be used as close to the furnace hot zone as possible to minimize electrical interference.

The lead wires should use the same kind of wire as the wire electrodes. If the lead wires and the wire electrodes use different wire, the types of lead wire shall be reported in the test report.

6.6 Caliper

Use a caliper as specified in ISO 3599 or ISO 6906.

6.7 Micrometer

Use a micrometer in accordance with ISO 3611 or another suitable measuring device for measuring the dimensions of the test piece and the distance between voltage terminals with a resolution of ± 0,01 mm.

7 Test piece

7.1 Shape and dimensions

The shape and dimensions shall be determined with an uncertainty of not more than ± 0,15 %.

a) A test piece should be prepared by cutting from a commercial product or a laboratory-made test piece fabricated under the similar conditions as the commercial product. The dimensions should be 4 mm × 3 mm × 35 mm or larger, typically 4 mm × 3 mm × 40 mm. Rounding of the edge, or chamfering, is not necessary.

b) If the test piece cannot be made, the test piece should have a minimum length of 20 mm and a section of typically 4 × 3 mm, and this shall be reported in the test report.

7.2 Surface roughness

The surface roughness of the test piece, which shall be measured with a stylus-type instrument (see EN 623-4) should be less than 0,20 µm. If the surface roughness is not less than 0,20 µm, this shall be reported in the test report.

7.3 Density

The bulk density of the test piece shall be measured in accordance with ISO 18754 and reported.

7.4 Configuration of four wire electrodes

All four wire electrodes on a test piece, especially the current terminals (hc and lc in Figure 2), shall possess high reversibility for the conductive ceramics. The voltage terminals (hp and lp in Figure 2) shall be fabricated with a minimum spacing of 10 mm (whenever possible, 20 mm) in the centre of the test piece. The width of a terminal should be as narrow as possible and less than 1 mm. Current terminals shall be placed at least 5 mm away from voltage terminals and should be fabricated on both edges of the test piece with a wide area.

Conductive paste, such as Pt, Au and Ag, that is not chemically reactive with the test piece and has similar conductivity to the wire electrodes, can be applied to reduce contact resistance between the test piece and the wire electrodes.

7.5 Number of test pieces

The number of test pieces shall be at least three.

8 Test procedure

8.1 Dimension measurement of a test piece

The cross-sectional area (A) of a test piece shall be calculated from the width and thickness of the test piece by using the caliper specified in ISO 3599 or ISO 6906, or the micrometer specified in ISO 3611. The width and thickness will be measured with an uncertainty of not more than 1 %. The distance between the voltage terminals (L) is defined as the distance between the central positions of the voltage terminals and shall be measured by using the caliper with an uncertainty of not more than 1 %.

8.2 Heating of a test piece

Tests shall use a furnace with a hot zone of uniform temperature in which the entire test piece can be placed. The following conditions shall be also satisfied:

a) Permissible tolerance of temperature of the test piece shall be ± 2 °C at temperatures between 0 °C and 500 °C, and ± 3 °C at temperatures between 500 °C and 1 000 °C.

b) The effects of electromagnetic noise produced by the electric furnace shall be adequately minimized. To achieve this, it is recommended that a DC power supply is used or a non-inductive coil heater if an AC power supply is used.

The thermal expansion coefficient of the test specimen can be measured as a means to correct the length and the cross-sectional area of the test specimen according to ISO 17562. In this case, note that the data corrections for the thermal expansion are made on the dimensions of the sample in the test report using Formula (1):

$$L_T = L_0 + \Delta L = L_0 + \alpha L \Delta T \quad (1)$$

where

L_T is the length of the test piece at measured temperature;

ΔL is the change in the length, L, of the test piece;

L_0 is the length of the test piece at room temperature;

α is the coefficient of linear thermal expansion;

L is the length of the test piece;

ΔT is the temperature change of the test piece.

8.3 Maintenance of gas composition and gas flow rate

During the measurement, the steady-state gas flow at a fixed gas composition and flow rate shall be maintained by using mass flow controllers or gas flow-controlling apparatus. Alternatively, a premixed or pure gas can be used to keep a fixed gas composition during the measurement. The gas composition and its flow rate shall be calibrated during or before the measurement. The method for the calibration shall be in accordance with the ISO 6145-7.

8.4 Measurement of total electrical conductivity

Measurement shall be done as follows:

a) Start measurement after the appropriate time has passed since the test piece reached the test temperature.

b) Choose a maximum current (I_{max}) in the range 10 mA to 100 mA.

c) Record the voltage values between the voltage terminals for at least four current values (I_1, I_2, I_3, I_4) equally spaced between $-I_{max}$ and $+I_{max}$. The values of each voltage (V_1, V_2, V_3, V_4) should be measured to a precision of three significant digits.

d) Repeat the measurements at least three times (ideally five times) to reduce any uncertainty.

e) Plot the obtained values in a I-V plot. If any marked deviation from linearity is observed, discard the results, check the test set-up and repeat the measurement from b). In this case, the *I*-*V* result shall be reported in the test report.

9 Calculation of total electrical conductivity

The total electrical conductivity shall be calculated using Formula (2):

$$\bar{\sigma} = \frac{\Sigma \sigma_n}{n}, \sigma_n = \frac{L}{R_n \times A} = \frac{I_n \times L}{V_n \times A} \tag{2}$$

where

$\bar{\sigma}$ is the average total electrical conductivity (S cm^{-1});

n is the number of measurements equally spaced between $-I_{max}$ to $+I_{max}$, at least four;

σ_n is the n^{th} total electrical conductivity value (S cm^{-1});

L is the distance between two inner terminals (cm);

R_n is the resistance (Ω);

A is the cross-sectional area of the test piece (cm^2);

I_n is the n^{th} applied DC (A);

V_n is the n^{th} measured voltage (V).

