INTERNATIONAL STANDARD

ISO 11894-1

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Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for conductivity measurement of ion-conductive fine ceramics —

Part 1: **Oxide-ion-conducting solid electrolytes**

Céramiques techniques — Méthode d'essai pour le mesurage de la conductivité des céramiques techniques conductrices d'ions —

Partie 1: Électrolytes solides conducteurs d'ions oxydes

Reference number
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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 11894-1 was prepared by Technical Committee ISO/TC 206, *Fine ceramics*.

ISO 11894 consists of the following parts, under the general title *Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for conductivity measurement of ion-conductive fine ceramics*:

— Part 1: Oxide-ion-conducting solid electrolytes

Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for conductivity measurement of ion-conductive fine ceramics —

Part 1: Oxide-ion-conducting solid electrolytes

1 Scope

This International Standard describes a test method for the determination of ionic conductivity of oxide-ion-conducting solid electrolytes by the 4-terminal method with alternating current (AC 4-terminal method).

This International Standard applies to solid electrolytes which have oxide ionic transference numbers higher than 0,99. The applicable conductivity range shall be 1 to 1,000 S m^{-1}.

Values expressed in this International Standard are in accordance with the International System of Units (SI).

2 Normative references

The following referenced documents are indispensable for the application 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 80000-1, *Quantities and units — Part 0: General*

ISO 554, *Standard atmospheres for conditioning and/or testing — Specifications*

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

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

ISO 4287, *Geometrical Product Specifications (GPS) — Surface texture: Profile method — Terms, definitions and surface texture parameters*

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

ISO 14704, *Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for flexural strength of monolithic ceramics at room temperature*

ISO 15165, *Fine ceramics (advanced ceramics, advanced technical ceramics) — Classification system*

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

3 Terms and definitions

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

3.1
ionic conduction
electrical conduction where ions carry the electrical charges

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

3.3
ionic transference number
ratio of ionic conductivity relative to total conductivity, which is the sum of ionic conductivity and electronic (hole) conductivity

Note 1 to entry: The region in which an ionic transference number is higher than 0,5 is defined as the ion conduction region, and the region in which an ionic transference number is higher than 0,99 is defined as the electrolytic conduction region.

3.4
oxide ion conductor
a substance whose electrical conduction is primarily governed by ionic conduction of oxide ion

Note 1 to entry: In this standard, the term indicates an oxide solid electrolyte with an oxide ion transference number higher than 0,99.

3.5
AC 4-terminal method
method for measuring electrical conductivity using AC (Figure 1)

Note 1 to entry: In this method, four electrodes are attached onto a test piece. The two outer electrodes which are called current terminals supply AC to the test piece. The two inner electrodes which are called voltage terminals measure the voltage. The electrical conductivity is determined with the applied current, the voltage measured and the geometry of the test piece.

3.6
reversible electrode
electrode where the ionic species acting as the charge carrier can be injected into or removed from the test piece rapidly enough to give a negligibly small polarization at a supplied current

3.7
Bode diagram
diagram showing the complex impedance of materials by plotting the logarithm of the absolute value of impedance and the phase of impedance on the ordinate as a function of the logarithm of the frequency on the abscissa

3.8
common mode voltage
in an impedance measurement using an AC 4-terminal method, the voltages generated between *H*p and *L*c, and between *L*p and *L*c, voltages which have the same amplitude and the same phase

Note 1 to entry: In the measurement described in this standard, this voltage corresponds to the voltage between the *L*p-*L*c terminals in Figure 2.

4 Symbols

The symbols used throughout this International Standard and their designations are given in Table 1.

Table 1 — Symbols

Symbol	Unit	Definition
σ	S m^{-1}	Ionic conductivity
L	m	Distance between voltage terminals
R	Ω	Effective resistance value
A	m^2	Test-piece cross-sectional area
Z	Ω	Impedance

5 Test piece

5.1 Shape and dimensions

A test piece should be prepared by cutting from a commercial product or a laboratory-made specimen which is fabricated under the similar conditions as the commercial product. The shape and dimensions should be in the dimensions of 4 mm x 3 mm x 36 mm or larger, typically 4 mm x 3 mm x 40 mm. Rounding of the edge, or chamfering is not necessary.

If the test piece mentioned above cannot be made, the shape and dimensions of the test piece shall be in accordance with the agreement between the parties involved.

5.2 Surface roughness

Surface roughness (*Ra*) of the test piece should be less than 0,20 µm. In the other cases out of this condition, the surface roughness shall be reported.

5.3 Density

Bulk density of the test piece shall be measured in accordance with ISO 18754.

5.4 Electrodes

5.4.1 Configuration of electrodes

All 4 electrodes on a test piece, especially the current terminals (hc and lc in Figure 2) shall possess high reversibility for the conductive oxide ion. The voltage terminals (hp and lp in Figure 2) shall be fabricated with a spacing of 20 mm in the centre of the test-piece. The width of a terminal should be as narrow as possible and shall be less than 2 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.

5.4.2 Preparation of electrodes

The electrodes for electro-active substances of gaseous species such as oxygen shall possess the porosity to supply them at the electrode/electrolyte interface.

The electrode layer can be fabricated by one of the following methods of applying/firing conductive paste, sputtering or vapor deposition. Platinum or silver should be selected as the electrode material. The choice of the electrode material should be performed taking the melting point into consideration. In the case of using a commercially available metal paste composed of metal particles, it is strongly recommended not to use the pastes containing inorganic components as binder, particularly silica-based flux. In order to maintain the reversibility of the oxygen exchange reaction at the electrode/electrolyte interface, the firing procedure should be optimized to ensure the appropriate porosity. After firing the electrodes, lead wires of the same metal as the electrodes should be wound onto the electrodes with the conductive paste. The test piece should be fired again to tightly fix the electrodes.

5.5 Number of test piece

The number of test piece shall be at least three.

6 Test procedure

6.1 Measurement of cross-sectional area of a test-piece and the distance between voltage terminals

Cross-sectional area of a test-piece (A) shall be determined by using the callipers specified in ISO 3599 or ISO 6906, or the micrometer specified in ISO 3611. The distance between voltage terminals (L) is defined as the distance between central positions of two terminals and shall be measured by using the calliper.

6.2 Conditions of testing

The testing should be done in the condition specified in ISO 554. The recommended temperature is 296 ± 2 K and the relative humidity is 50 ± 5 %.

6.3 Heating of a test piece

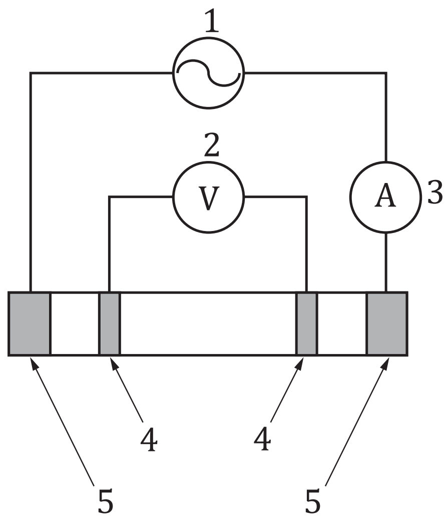
Testing shall use an electric furnace with a hot zone of uniform temperature in which the test piece can be entirely placed. The following conditions should also be satisfied:

a) Permissible tolerance of temperature of test piece is ±2 K at temperatures lower than 773 K, and ±3 K at temperatures between 773 K and 1273 K.

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

6.4 Method for measurement

Impedance of a test piece shall be measured by the AC 4-terminal method as shown in Figure 1. The oxide ion conductivity (σ) can be determined from the impedance measured.



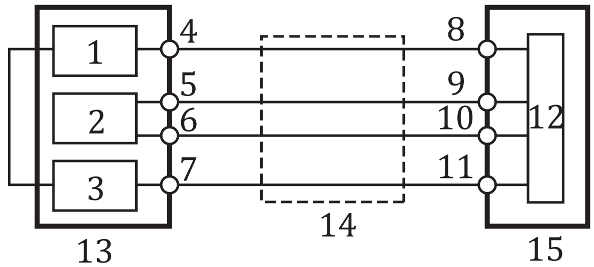
Key

1 Oscillator
2 Voltmeter
3 Amperemeter
4 Voltage terminal
5 Current terminal

Figure 1 — AC 4-terminal method

6.5 Measurement system

The measurement system shall be basically composed of an electric furnace in which a test piece is placed, an AC impedance meter and 4 lead wires as shown in Figure 2.



Key

1 AC Oscillator
2 Voltmeter
3 Amperemeter
4 *H*c (Current terminal)
5 *H*p (Voltage terminal)
6 *L*p (Voltage terminal)
7 *L*c (Current terminal)
8 *h*c (Current terminal)
9 *h*p (Voltage terminal)
10 *l*p (Voltage terminal)
11 *l*c (Current terminal)
12 Test piece
13 Measurement unit (AC impedance meter)
14 Lead wires for measurement
15 Electric furnace

Figure 2 — Measurement system

6.6 AC impedance meter

The AC impedance meter shall be capable of measurement using 4 terminals with a precision of at least 3 significant digits in the impedance range of measurement. In the measurement, the instrument shall satisfy the following conditions:

a) The input impedance of the voltage terminals (Hp and *L*p) shall be sufficiently greater than the impedance of the test piece, electrodes and lead wires. The input resistance shall be higher than 1 MΩ, and the input capacity shall be less than 20 pF.

b) In the AC 4-terminal measurement, the effect of the common mode voltage generated between *L*p and *L*c on the measured impedance should be smaller than 1 % of the measured impedance.

c) The voltage measurement of *H*p and *L*p shall be guaranteed for the operation within the range of measured voltage.

NOTE Some AC impedance meters limit their working voltages of *H*p and *L*p to protect and stabilize the circuits. If the voltages of *H*p and *L*p become too high, a large error will appear in these meters.

d) The instrument should have a function for correcting the effects from the lead wires.

e) The instrument should be able to measure absolute value of impedance and its phase, or the effective resistance and reactance.

6.7 Lead wires

The lead wires which connect between the instrument and the wires from electrodes on the test-piece and should be as short in length as possible to avoid influences from external noise and floating capacity. It is preferred to use coaxially shielded cables to as close to the furnace hot zone as possible to minimize electrical interference.

6.8 Preparation for measurement

Prior to the impedance measurement, the following procedure should be carried out to confirm the appropriateness of the system.

a) To eliminate the effects of lead wires on measurement, the correction should be made using the compensation function of the AC impedance meter.

b) To ensure the performance of the electrodes, the impedance should be measured between every two electrodes on the test piece by a 2-terminal method. One terminal is made by connecting the *H*c and *H*p terminals and the other is by connecting the *L*p and *L*c terminals. The impedances measured must be sufficiently small relative to the input impedance of the voltage terminals of the AC impedance meter being used.

c) To check the effects of common mode voltage in the AC 4-terminal method, the following connection should be made; *H*c to hc, *H*p and *L*p to lp and *L*c to lc, and measure the impedance of the test-piece. This impedance shall be sufficiently small relative to the value between hp and lp measured by the preceding method in b).

7 Measurement

Measurement shall be done as follows:

a) The voltage applied between the current terminals should be lower than 500 mV.

b) The recommended frequency is between 100 Hz and 10 kHz

c) Measure the absolute value of impedance ($|Z|$) and the phase (θ) between the voltage terminals. Measurement should be done using at least 3 frequencies of around 100 Hz, 1 kHz and 10 kHz. Only when the phases of the measured impedance are close to zero, the absolute value of impedance should be measured to a precision of 3 significant digits and take the value as the effective resistance (R).

d) Measurement should be started after the test-piece reaches the test temperature at an appropriate time intervals, and the measured effective resistance which has become constant should be adopted as a stationary value. If a stationary value cannot be measured due to slow relaxation, the tentative value should be reported with the heating procedure until the impedance measurement.

8 Calculation of oxide ion conductivity

The oxide ion conductivity shall be calculated using the following formula:

$$\sigma = \frac{L}{R \times A} \tag{1}$$

where

σ is the oxide ion conductivity ($S\ m^{-1}$);

L is the distance between voltage terminals (m);

R is the effective resistance (Ω);

A is the cross-sectional area of the test-piece (m^2).

9 Expression of oxide ion conductivity

9.1 Oxide ion conductivity

The obtained oxide ion conductivities shall be averaged and rounded to 2 significant digits, according to ISO 80000-1.

9.2 The expression of oxide ion conductivity

a) The measurement temperature and the oxide ion conductivity with the phase shall be described.

b) A Bode diagram should be used when the measurements are performed at various frequencies.

c) To describe the temperature dependence of oxide ion conductivity, the logarithm of the conductivity should be plotted on the ordinate as a function of the reciprocal of the absolute temperature on the abscissa. The data points should be connected with a straight line.

10 Test report

The test report shall include the following items:

a) the measured materials and their manufacturer

b) shape of the test-piece and their fabrication method

c) storage condition of the test-piece before measurement (time, humidity and temperature)

d) temperature and humidity of the test room

e) dimensions, bulk density and number of test piece

f) fabrication of the electrodes (material and fabrication method)

g) temperature of the test piece during measurement, and the atmosphere around the test piece

h) oxide ion conductivity measured (conductivity and phase). In the case that a stationary value cannot be obtained, the heating procedure until the impedance measurement shall be reported

i) the date of the test

j) other remarks if necessary

ICS 81.060.30

Price based on 8 pages