INTERNATIONAL STANDARD

ISO 16773-4

First edition
2009-05-01

Paints and varnishes — Electrochemical impedance spectroscopy (EIS) on high-impedance coated specimens —

Part 4:
Examples of spectra of polymer-coated specimens

Peintures et vernis — Spectroscopie d'impédance électrochimique (SIE) sur des éprouvettes revêtues de haute impédance —

Partie 4: Exemples de spectres d'éprouvettes revêtues de polymères

Reference number
ISO 16773-4:2009(E)

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Page

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 16773-4 was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*, Subcommittee SC 9, *General test methods for paints and varnishes*.

ISO 16773 consists of the following parts, under the general title *Paints and varnishes — Electrochemical impedance spectroscopy (EIS) on high-impedance coated specimens*:

— *Part 1: Terms and definitions*

— *Part 2: Collection of data*

— *Part 3: Processing and analysis of data from dummy cells*

— *Part 4: Examples of spectra of polymer-coated specimens*

Paints and varnishes — Electrochemical impedance spectroscopy (EIS) on high-impedance coated specimens —

Part 4: Examples of spectra of polymer-coated specimens

1 Scope

This part of ISO 16773 gives some typical examples of impedance spectra of high-impedance coated metal samples. Some guidance on interpretation of such spectra is also given.

2 Theoretical background

2.1 Basic considerations

A basic introduction to electrochemical impedance spectroscopy, especially in connection with corrosion, is given in ASTM G 106.

It is not intended to limit the interpretation of EIS measurements to the models given below. Other interpretations may be valid. The choice of the proper model requires other experimental and theoretical considerations to be taken into account.

2.2 Examples of models

2.2.1 Purely capacitive coating

A metal covered with an undamaged coating generally has a very high impedance. The equivalent circuit for such a situation is shown in Figure 1.

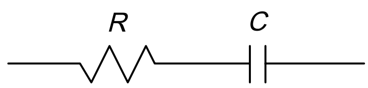
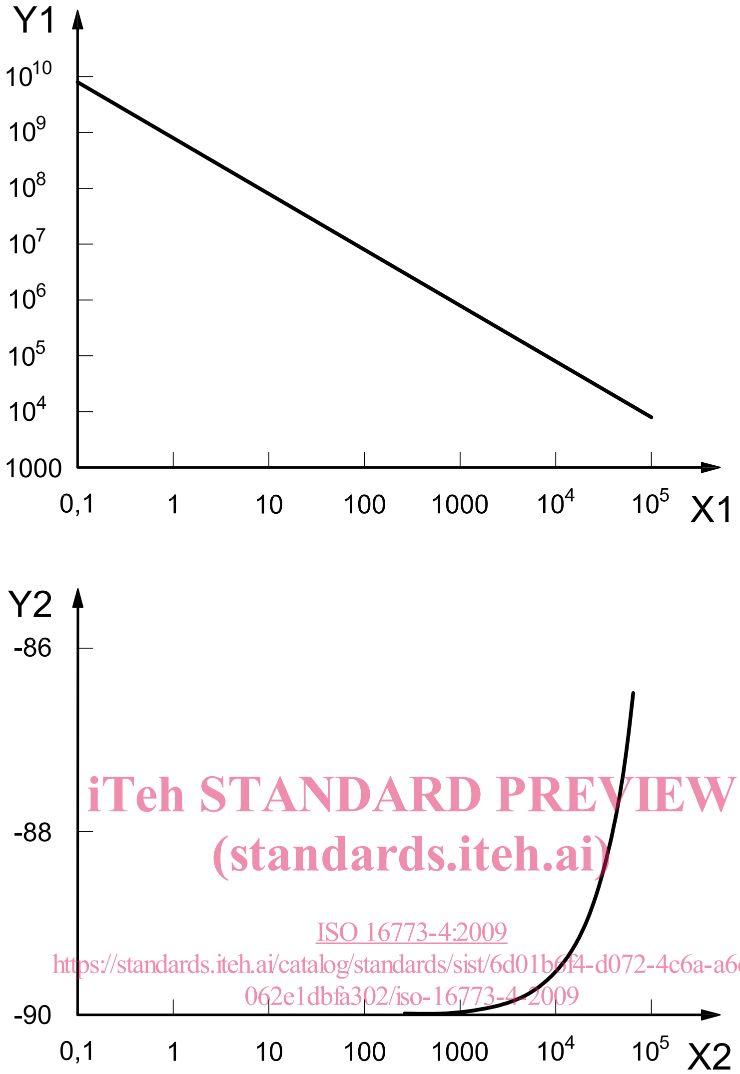


Figure 1 — Equivalent circuit for a purely capacitive coating

The model includes a resistor representing the resistance R of the solution and, connected in series with it, a capacitor representing the capacitance C of the coating.

In practice, the resistance of a perfect coating can often not be seen in the given frequency range. Any deviation from the graph given in the Bode plot in Figure 2 indicates either a modified model or the input limits of the impedance device (see Annex A of ISO 16773-2:2007).



Key

X_1 frequency f, in Hz
Y_1 impedance Z, in Ω
X_2 frequency f, in Hz
Y_2 phase angle φ, in degrees

Figure 2 — Bode plot for a perfect coating

2.2.2 Randles equivalent circuit

The Randles equivalent circuit includes the resistance of the solution R_S, the capacitance of the coating C_C and the ohmic resistance of the coating R_C, as shown in Figure 3.

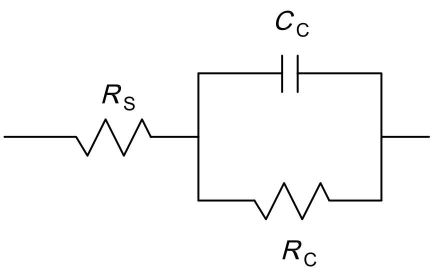
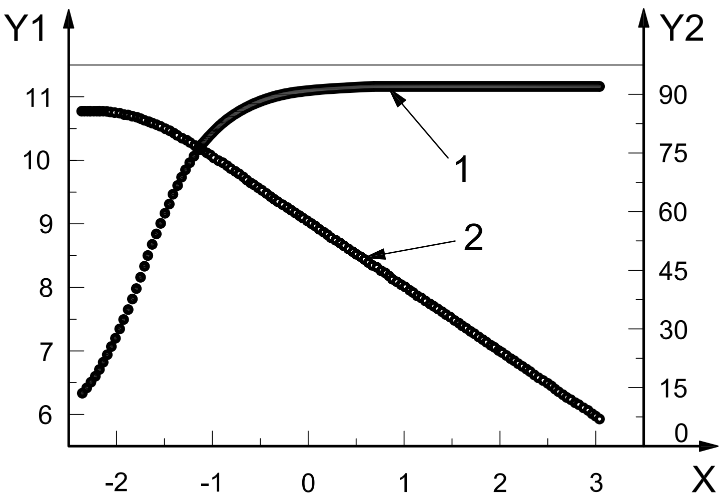


Figure 3 — Randles equivalent circuit

The Bode plot for a Randles equivalent circuit is shown in Figure 4.



Key

X log*f* (*f* in Hz)

Y_1 log|*Z*| (*Z* in Ω)

Y_2 |*φ*| (degrees)

1 phase angle *φ*

2 impedance *Z*

Figure 4 — Bode plot for a Randles equivalent circuit

2.2.3 Extended Randles equivalent circuit

Quite often, fitting experimental data to the model shown in Figure 3 results in systematic errors. In such cases, the literature shows that it is possible to use the model shown in Figure 5 to obtain a better fit.

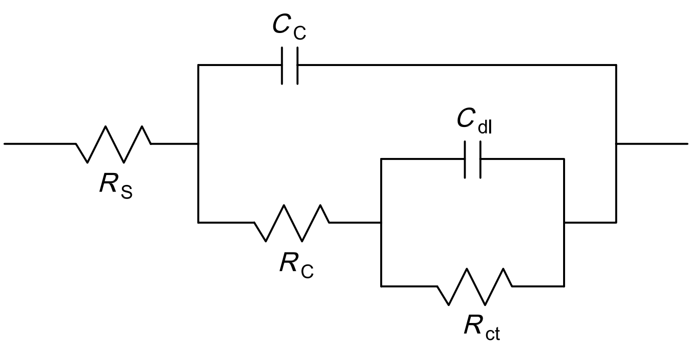
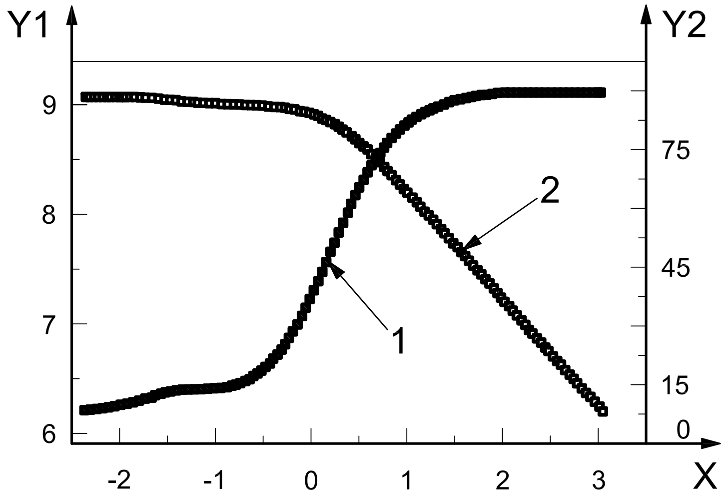


Figure 5 — Extended Randles equivalent circuit

NOTE This model is not necessarily the most appropriate and other models are not excluded.

In the case of high-impedance coatings, the charge-transfer resistance R_{ct} and double-layer capacitance C_{dl} in the extended Randles circuit correspond to properties of the coating rather than to corrosion processes in the underlying metal.

The Bode plot shown in Figure 6 clearly shows the additional contribution of these two added elements. Again, the Bode plot does not go high enough in frequency to measure the solution resistance. In practice this is not a problem, because the solution resistance is a property of the test solution and the test cell geometry, not a property of the coating.



Key

X log$f$ (f in Hz)

Y_1 log$|Z|$ (Z in Ω)

Y_2 $|\varphi|$ (degrees)

1 phase angle φ

2 impedance Z

Figure 6 — Bode plot for an extended Randles equivalent circuit

Annex A
(informative)

Examples

A.1 General

This annex contains a collection of spectra obtained from materials described briefly in the relevant clause. The examples were obtained from various laboratories using a range of different equipment and materials.

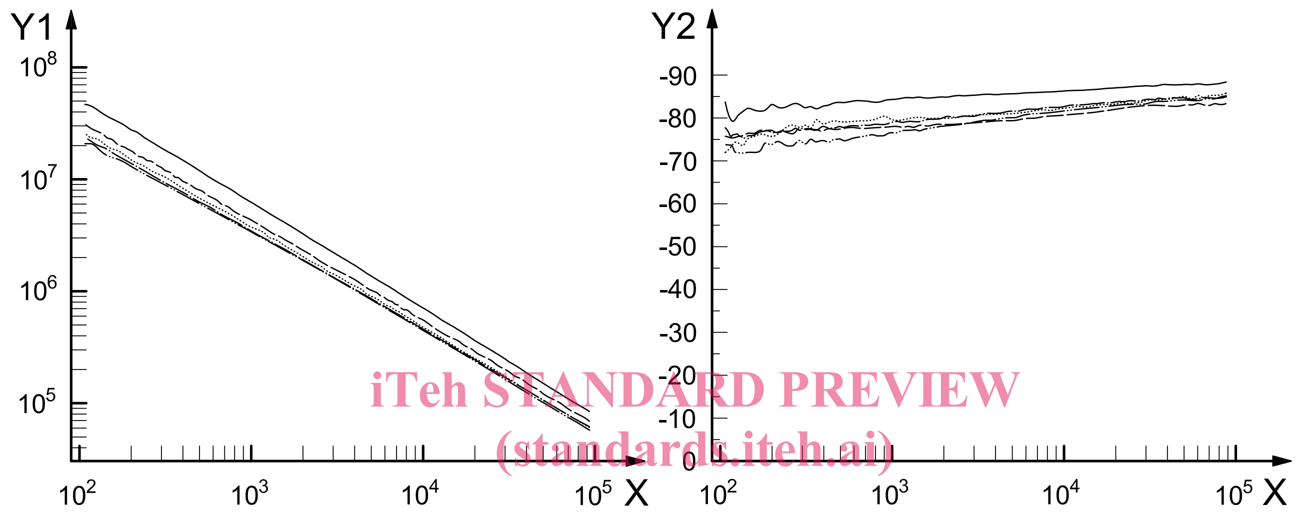
This collection of spectra is not intended to imply that all the materials mentioned necessarily give spectra similar to those shown or that the spectra given here are free of experimental errors. The collection does not represent the complete range of coating materials.

A.2 Example 1

This example shows how a smaller than usual thickness of a high-build coating material can be used to investigate the influence of immersion time on EIS measurements.

Details: Two-component epoxy coating, typically used for (maritime) steel constructions, above and below the water level. Airless spray application. DFT (dry film thickness) recommended by the manufacturer: 1 000 µm to 3 000 µm.

Measurements were performed on one coat on steel, DFT 200 µm, on an area of 10 cm^2 at 21 °C using concentrated artificial rainwater (see Annex B). A vertical three-electrode set-up, with a saturated Ag/AgCl reference electrode, was used. Spectra were recorded after defined periods of immersion.



Key

X frequency f, in Hz

Y_1 modulus of the impedance $|Z|$, in Ω·cm^2

Y_2 phase angle φ, in degrees

———— t = 0 h

– – – – t = 2 h

.... t = 24 h

—·—·— t = 168 h

—··—··— t = 503 h

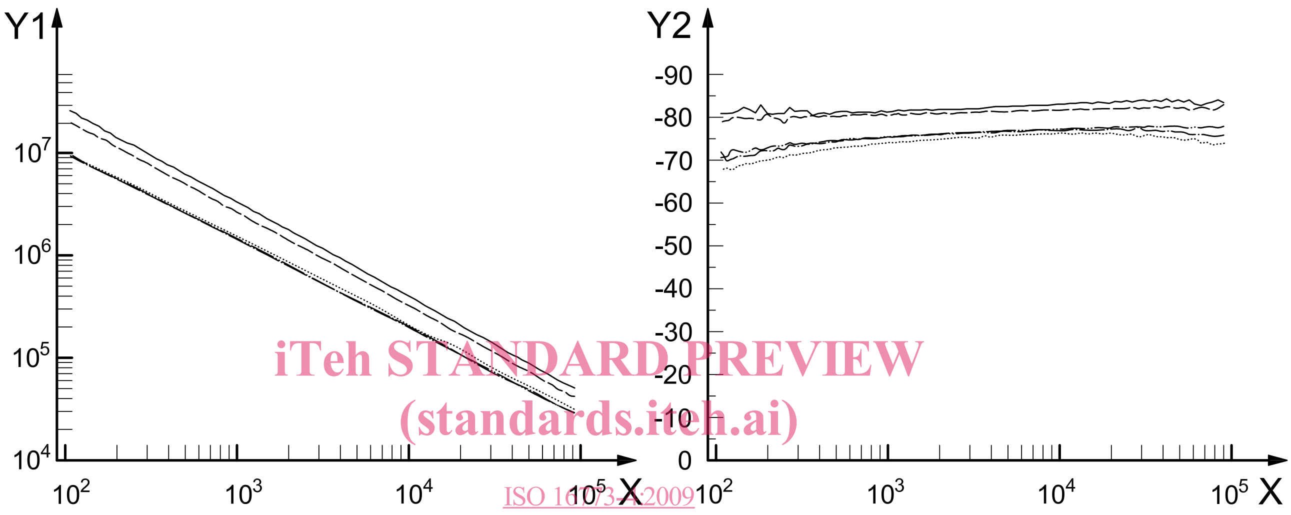
Figure A.1 — Bode plot for a high-build coating material under immersion conditions

A.3 Example 2

This example concerns a surface-tolerant coating material which does not require the same amount of surface pretreatment as that in Example 1. Usually, derusting with mechanical tools is used rather than grit blasting.

Details: Surface-tolerant two-component epoxy coating for (maritime) steel constructions, above and below the water level. Can be applied on corroded steel, grit-blasted steel and old (undamaged) paint coatings. Application by airless spray, conventional spray, brushing or rolling. DFT recommended by the manufacturer: 100 µm to 200 µm.

Measurements were performed on one coat on steel, DFT 250 µm, on an area of 10 cm^2 at 21 °C using concentrated artificial rainwater (see Annex B). A vertical three-electrode set-up, with a saturated Ag/AgCl reference electrode, was used. Spectra were recorded after defined periods of immersion.



Key

X frequency f, in Hz

Y_1 modulus of the impedance $|Z|$, in $\Omega \cdot cm^2$

Y_2 phase angle φ, in degrees

——— t = 0 h

– – – – t = 2 h

········ t = 24 h

—·—·— t = 168 h

—··—··— t = 502 h

Figure A.2 — Bode plot for a surface-tolerant coating material under immersion conditions