
**Corrosion of metals and alloys —
Multielectrode arrays for corrosion
measurement**

*Corrosion des métaux et alliages — Assemblages multi-électrodes
pour la mesure de la corrosion*

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Foreword

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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).

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This document was prepared by Technical Committee ISO/TC 156, *Corrosion of metals and alloys*.

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.

Introduction

Multielectrode array technology has been used to study electrochemical behaviours and the localized corrosion of metals and alloys since the 1970s^[1] to ^[5]. It has been demonstrated that multielectrode arrays are highly powerful tools for studying the spatiotemporal behaviour of metals in laboratories^[2] to ^[16] and for monitoring non-uniform corrosion, especially localized corrosion in laboratories and plants^[17]. Multielectrode arrays are also used as high throughput probes for studying the statistical behaviour of metal corrosion^{[1][18]} and for the evaluation of inhibitors^[19].

This document is designed to outline the requirements and procedures for conducting corrosion measurements using multielectrode arrays.

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Corrosion of metals and alloys — Multielectrode arrays for corrosion measurement

1 Scope

This document specifies the methodology of using multielectrode arrays for the measurement of the corrosion, especially localized corrosion, of metals and alloys. It can be used as a powerful tool for studying the initiation and propagation processes of localized corrosion. It is also a useful tool for long-term corrosion monitoring in the field, especially for localized corrosion, and for obtaining high throughput results for the evaluation of metals with different compositions and/or physical properties in different environments and the screening of a large number of inhibitors. Additionally, the galvanic coupling current and potential distribution of dissimilar metal pairings can be assessed by multielectrode arrays. Multielectrode arrays can be implemented in full-immersion, thin-film, spray and alternating wet-dry cycle exposures.

This document is not intended to be used for measurements of corrosion caused by a non-electrochemical mechanism.

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 8407, *Corrosion of metals and alloys — Removal of corrosion products from corrosion test specimens*
ISO 23449:2020
https://standards.iteh.ai/catalog/standards/sist/d047a596-34e7-4586-8a08-18ff52df2d8/iso-23449-2020

ISO 8044, *Corrosion of metals and alloys — Vocabulary*
ISO 23449:2020

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 8044 and the following 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

uneven general corrosion

corrosion that occurs over the whole exposed area of a metal at different rates across the exposed area

Note 1 to entry: It is a type of general corrosion, as defined in ISO 8044, that produces an uneven or wave-like surface^{[20][21]} where the thickness reduction at the more corroded areas is significantly larger than the thickness reduction at the less corroded areas or the average corroded areas.

3.2

non-uniform corrosion

corrosion that occurs at different rates over a metal surface where there is a localized surplus of net anodic or net cathodic rates such that a localized area does not exhibit charge neutrality and electrons flow within the metal from the anodic-dominant areas to the cathodic-dominant areas

Note 1 to entry: Non-uniform corrosion includes both localized corrosion, as defined in ISO 8044, and *uneven general corrosion* (3.1). Non-uniform corrosion also includes the type of general corrosion that produces even surfaces at the end of a large time interval, but uneven surfaces within small time intervals.

3.3 multielectrode array

device consisting of multiple electrodes for corrosion studies and corrosion monitoring

Note 1 to entry: The electrodes in a multielectrode array can either be arranged in an organized pattern on a 2D plane or packed randomly on a 2D plane or in a 3D space. When the electrodes are randomly packed, the word "array" in the term means that there are many electrodes in the device.

3.4 zero-voltage ammeter

ZVA

ammeter that imposes a negligibly low voltage drop when inserted into a circuit for measurement of current

Note 1 to entry: When a ZVA is used to measure the coupling current between two electrodes, the two electrodes are essentially at the same potential.

Note 2 to entry: Both a *zero-resistance ammeter* (3.5) and a simple device formed with a shunt resistor and a voltmeter can be used as the ZVA providing they do not impose a significant voltage drop (< 1 mV) in the current-measuring circuit.

3.5 zero-resistance ammeter

ZRA

zero-voltage ammeter (3.4) that has a near zero dynamic resistance when inserted into a circuit for measurement of current

Note 1 to entry: ZRA is usually built with operational amplifiers and may impose a voltage between 50 μ V and 2 mV in the current-measuring circuit.

Note 2 to entry: When the measured current is in the nanoampere range or lower as often found in the *multielectrode arrays* (3.3), the ZRA's static resistance determined with Ohm's Law (ratio of voltage to current) is usually higher than 50 000 ohm, even though its dynamic resistance (derivative of voltage to current) is near zero ohm.

3.6 coupled multielectrode array

CMA

multielectrode array (3.3) whose electrodes are coupled together by wires or through the use of a multichannel *zero-voltage ammeter* (3.4) between the electrodes and the coupling joint so that all the electrodes connected to the coupling joint are essentially at the same potential

3.7 coupled multielectrode array sensor

CMAS

coupled multielectrode array (CMA) (3.6) that is used as a sensor for corrosion monitoring

Note 1 to entry: The outputs of a typical CMAS are usually simple parameters such as maximum corrosion rate and maximum penetration depth, while the outputs of a typical CMA are usually the large number of currents and/or potentials from all the electrodes.

3.8 cathodic protection effectiveness margin

cathodic protection margin of effectiveness

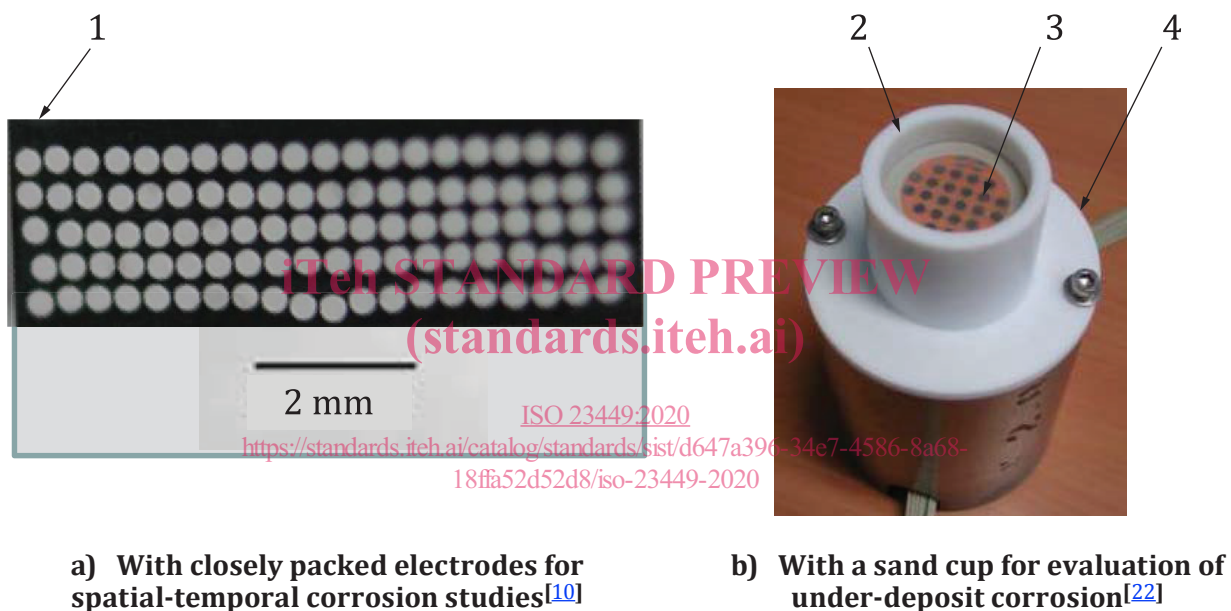
CPEM

degree of cathodic protection derived from the current of a *coupled multielectrode array sensor* (3.7) that has a value of 0 % when the cathodic protection starts to be adequate in terms of acceptable corrosion rate (e.g. 0,01 mm/a or 0,0 mm/a), and a value of 100 % when excessive hydrogen evolution starts

4 Principle

4.1 Multielectrode arrays

One of the characteristics of non-uniform corrosion, especially localized corrosion, on a metal surface is that there are some small areas that are more anodic and some small areas that are less anodic or that are cathodic. Multielectrode arrays, as shown in [Figure 1](#), are highly effective tools for studying non-uniform corrosion. In [Figure 1 a\)](#), the electrodes of the multielectrode array were closely packed in a 5×20 pattern to simulate the metal surface for studying the spatiotemporal behaviour of corrosion^[10]. In [Figure 1 b\)](#), the multielectrode array was buried under sands in a cup to evaluate under deposit corrosion^[22]. In general, the electrodes in a multielectrode array for spatial-temporal studies are arranged in regular patterns on a 2D plane, such as those shown in [Figures 1](#) and [2](#), and this type of multielectrode arrays are also called “wire beam electrodes”^{[2][13]}. The multielectrode arrays may also be arranged randomly on a 2D plane or 3D space ^{[1][18]}. In this case, the word “array” in the term means that there are many electrodes in the device.



Key

1	5 × 20 electrodes flush-mounted in epoxy	3	24 electrodes
2	sand-holding cup	4	heating device

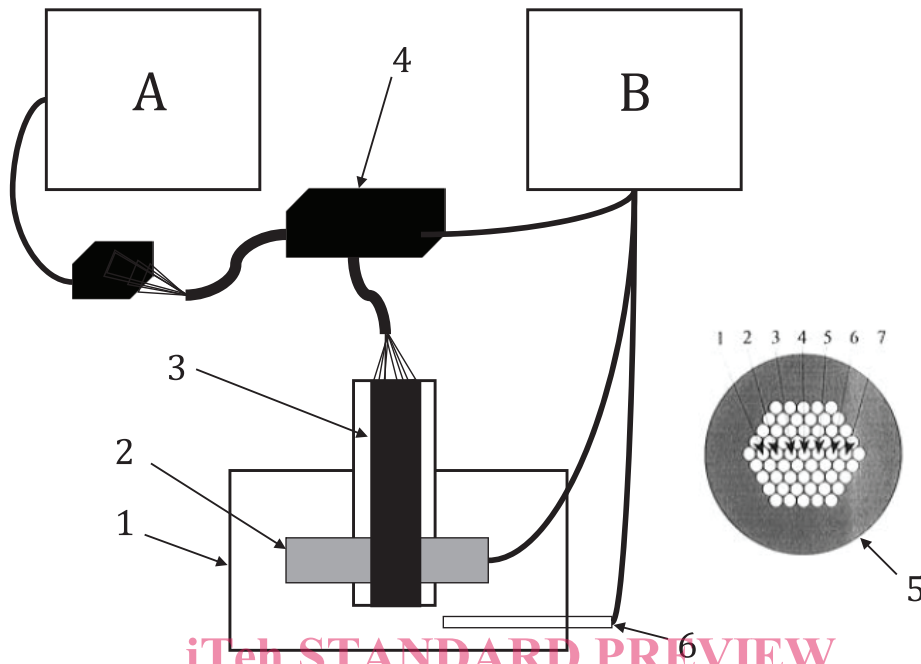
Figure 1 — Typical multielectrode arrays

The currents of the electrodes composing the array can be measured individually. It is possible to measure the potentials of each individual electrode, of a selected group of electrodes, or the totality of the electrodes if they are coupled (see below). It is at times technically feasible to polarize one or more electrodes using a single-channel potentiostat or a multi-channel potentiostat in order to evaluate the effects of polarization on the neighbouring electrodes^[10]. Because of the small size of the electrodes in the array, the polarization currents are usually very small (less than $1 \mu\text{A}$) and their effects on the measurements of the potential of the neighbouring electrodes due to the IR drop can be ignored.

4.2 Coupled multielectrode array (CMA)

If all the electrodes or a selected number of electrodes in a multielectrode array are coupled together by wires or through the use of multichannel ammeters that impose near-zero voltages between the electrodes and the coupling joint so that all the electrodes connected to the coupling joint are essentially at the same potential, such multielectrode array is called a “coupled multielectrode array (CMA)”. The ammeters that impose near zero voltage are called “zero-voltage ammeters (ZVAs)” and are described

in 5.2. Figure 2 shows a typical CMA system where all the electrodes are controlled at the same potential by the potentiostat through a multichannel ZVA box^[3].



- Key**
- A multichannel data acquisition system
 - B potentiostat
 - 1 electrochemical cell
 - 2 counter electrode
 - 3 CMA
 - 4 multichannel ZVA
 - 5 bottom view and electrode ID of the array
 - 6 reference electrode

NOTE 1 All electrodes are at the same potential.

NOTE 2 The counter electrode is electrically separated from the multielectrode array.

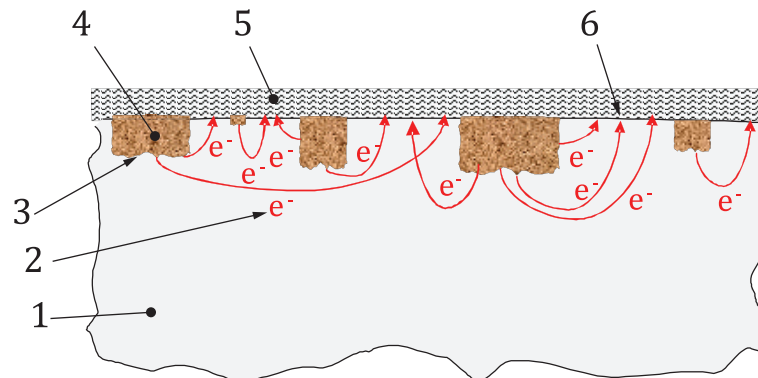
Figure 2 — Typical CMA system for electrochemical studies under polarization conditions^[3]

4.3 Multielectrode array with closely packed electrodes for studying spatiotemporal behaviour of localized corrosion

4.3.1 If the electrodes are arranged in an organized pattern such as 4 × 4, 5 × 20 or 10 × 10 and the electrodes are closely packed and their size are small (typically < 1 mm in diameter), such multielectrode array may be used to study the spatial and temporal behaviour of corrosion on a metal surface, e.g. when and where localized corrosion first initiates and how the localized corrosion propagates on the metal surface. Annex A shows a typical use of the CMA for studying the spatial and temporal behaviour of corrosion.

4.3.2 The CMA may also be used at its corrosion potential without any polarization. In a typical case of localized corrosion where there is clear separation of anodes and cathodes, the array simulates a one-piece metal section for which the electrodes that have net anodic currents simulate the anodic areas and the electrodes that have net cathodic currents simulate the cathodic areas on the metal surface as shown in Figure 3. By measuring the electron flow from the anodic electrodes to the cathodic electrodes on the

array as a function of time, the information of the initiation and propagation of localized corrosion that takes place on the metal under freely corroding conditions can be obtained.



Key

1	metal	4	corrosion products and electrolyte
2	electrons	5	corrosive electrolyte (liquid, thin, film or wet deposits)
3	anodic sites	6	cathodic sites

NOTE The electrons flow randomly in metal from anodic sites to cathodic sites. Cathodic reactions such as $O_2 + 4e^- + 2H_2O = 4OH^-$ occur at the cathodic sites. Anodic reactions such as $Fe - 2e^- + 2H_2O = Fe(OH)_2 + 2H^+$ occur at the anodic sites.

Figure 3 — Typical characteristics of localized corrosion on a metal surface at its corrosion potential — Electrons flow from anodic areas to the cathodic areas within the metal^[4]

In a typical non-uniform general corrosion case, there is no clear separation of anodes and cathodes, but some areas corrode more and some areas corrode less and all areas are anodic, at least for a short duration during corrosion process. The electrodes on the array that have net anodic currents simulate the more corroding areas and the electrodes that have net cathodic currents simulate the less corroding areas.

4.4 Coupled multielectrode array sensor (CMAS)

4.4.1 CMAS for corrosion monitoring

If a CMA is used as a sensor for corrosion monitoring, such a CMA is called a “coupled multielectrode array sensor (CMAS)”. [Figure 4](#) shows some typical CMASs. Unlike a CMA for spatial studies, a CMAS for field applications usually has fewer electrodes [see [Figure 4 a](#)] and the electrodes can be randomly packed [see [Figure 4 b](#)]. There is no need for a plant operator to know all the individual currents and create a corrosion map for a sensor in the fields. It often suffices for the operator to know the maximum corrosion rate, at the worst corroding area, and the associated maximum penetration depth, without needing to know where exactly these worst areas are. The outputs of the CMAS probes are often those two simple parameters: maximum corrosion rate (calculated from the most anodic current, which is from the worst or most corroding electrode) and maximum penetration depth (calculated from the most corroded electrode). The operators can apply their corrosion mitigation measures (e.g. by adding a corrosion inhibitor) based on the maximum corrosion rate. On the other hand, the engineers may decide how often the plant equipment should be inspected based on the maximum penetration depth (see ASTM G217-16 for additional information^[36]).