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MICROELECTRODES. DEFINITIONS, CHARACTERIZATION, AND APPLICATIONS

(Technical Report)

Prepared for publication by

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Microelectrodes. Definitions, characterization, and applications (Technical Report)

Abstract: Theory, preparation, and applications of microelectrodes and microelectrode arrays are critically reviewed, and future trends in the field are outlined. An operational definition of a microelectrode is also recommended.

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1. INTRODUCTION

If the geometric dimensions of a voltammetric working electrode become progressively smaller then the behavior of the electrode begins to depart from that of a large electrode which can be approximated by an electrode of infinite dimension. These differences are caused by changing conditions of the mass transport from the bulk of solution toward the electrode and have several important practical implications, such as a decreased ohmic drop of potential, IR , fast establishment of a steady-state signal, a current increase due to enhanced mass transport at the electrode boundary, and increased signal-to-noise ratio. These effects make sufficiently small electrodes advantageous in many areas of electroanalytical chemistry. The beneficial properties of small electrodes have been recognized since the time of rigorous description of mass transport in the vicinity of voltammetric electrodes but only during the early 1980s, when the development in microelectronics technology made it possible to measure reliably very low currents and to construct reproducibly very small electrodes, did their intense study and application begin. The application of small-size electrodes was further enhanced by increasing demands from analytical chemistry (e.g., the need for electrodes in miniature cells in detection for high-performance separations or in electrochemical sensors) and biochemistry (*in situ* electroanalytical measurements on living organisms).

These small-size electrodes have been called microelectrodes. The term “ultramicroelectrode” is also often used in the literature, but, to maintain the terminology consistent, it is preferable to stick to the more logical term, “microelectrode”. It is now conventionally assumed that a microelectrode has dimensions of tens of micrometers or less, down to submicrometer range, such as with the recently prepared carbon multi-wall nanotube electrode which is ca. 100 nm in diameter [1]. Microelectrodes of various geometries have been prepared mechanically or lithographically. In addition to single electrodes, microelectrode arrays have been prepared and used. This paper deals exclusively with voltammetric microelectrodes, as the performance of small-size potentiometric and reference electrodes does not differ from that of normal-size electrodes. An article of the present length cannot systematically

cover practical applications of microelectrodes. Therefore, typical examples are only given, and the reader is referred to the extensive review literature cited [2–15] for more detailed accounts.

2. PROPERTIES OF MICROELECTRODES

2.1 Theoretical aspects.

2.1.1 Single microelectrode

The basic types of microelectrodes and their arrays are shown in Fig. 1.

The most important factor determining the behavior of an electrode is the mass transport in solution in the vicinity of the electrode. When considering an uncomplicated charge-transfer reaction, then the voltammetric current signal is proportional to the flux of the electroactive substance toward the solution–electrode interface described by Fick's first law. Fick's second law then describes the time-dependent changes in the concentration of the substance amount caused by the flux—the partial derivative of the concentration with respect to time equals the divergence of the flux vector.

When the electrode potential is switched from a value at which no electrode reaction occurs to that corresponding to the limiting current of the electrode reaction, then the concentration of the electroactive substance at the electrode surface decreases to zero and a concentration gradient develops over a certain distance from the electrode surface into the bulk of the solution; this distance increases with increasing electrolysis time. The solution volume within which the diffusional flux of the substance occurs is termed the diffusion layer. The flux of the substance toward the electrode is then described by the product of the diffusion coefficient of the substance, D , and its bulk concentration divided by the diffusion layer thickness, δ . This quantity is defined, for planar semi-infinite diffusion, by the relationship

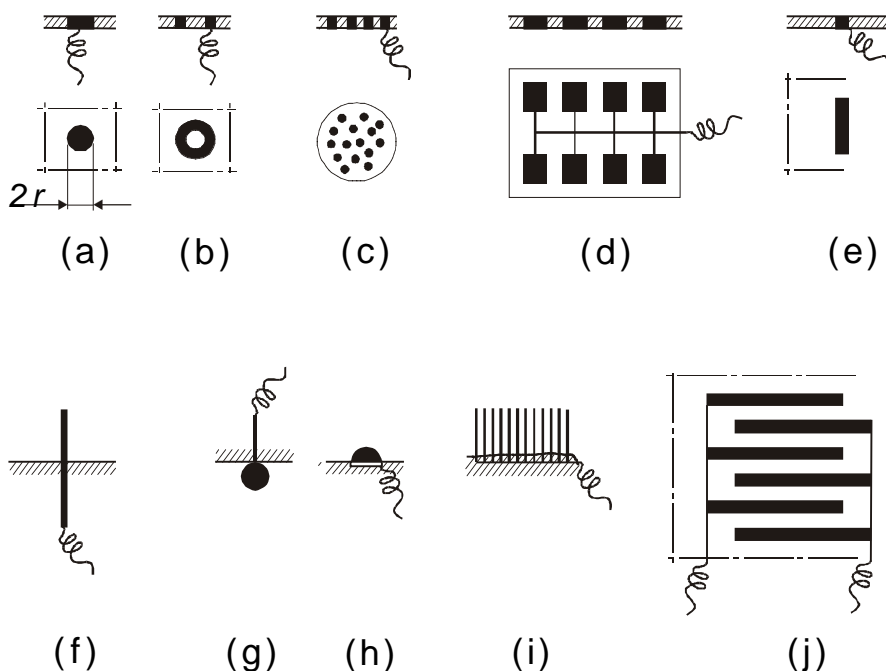


Fig. 1 Most important geometries of microelectrodes and microelectrode arrays: (a) microdisk, (b) microring; (c) microdisk array (a composite electrode); (d) lithographically produced microband array; (e) microband; (f) single fiber (microcylinder); (g) microsphere; (h) microhemisphere; (i) fiber array; (j) interdigitated array.

$$\delta = \sqrt{\pi Dt} \quad (1)$$

and this definition is used in the text below. The diffusion layer thickness can be rigorously calculated for a spherical electrode and for a planar disk electrode placed in a plane of an insulator; the formulae for electrodes with other geometries are approximations that differ in dependence on the initial assumptions.

If the electrode geometry is approximated by the model of an infinitely large planar electrode with the substance flux perpendicular to the electrode plane, then the flux is uniform over the entire electrode surface and the substance concentration attains the bulk value at a distance of a few diffusion layer thickness values. However, the flux is not uniform over the electrode surface (edge effect) for other geometries. For example, if a convex electrode is embedded in a planar insulator, then the size of the electrode can be described by twice the linear dimension of the electrode (e.g., $2r$, where r is the radius of a disk or hemispherical electrode). Two limiting cases can then be distinguished, namely, δ is much smaller than r and δ is much larger than r .

For $\delta \ll r$, the perturbation of the linear diffusion flux caused by the hemispherical diffusion at the electrode edges extends to a short distance of several δ from the edge. Thus, only a small part of the electrode surface is affected, and the behavior of the electrode can be approximated by the infinite electrode model.

For $\delta \gg r$, the edge effect plays a predominant role, and the diffusional flux toward the electrode is constant with time but inhomogeneous over the electrode surface; it increases with decreasing distance from the electrode edge. Concentration of the electroactive substance attains the limiting value described by the equation for steady-state transport, which corresponds to the time derivative being zero in Fick's second law.

An extremely important conclusion follows from the effects described above, namely, that the diffusion layer thickness depends on time. Therefore, the differentiation between the two cases considered above also depends on time. At a sufficiently short time, any planar electrode, no matter how small (with the obvious limitations of the diffusion model), behaves as an infinitely large planar electrode. With increasing time, the electrode behavior gradually changes toward the second case. In fact, a single dimensionless parameter, δ/r , is sufficient for describing the electrode behavior.

After sufficiently long time, a steady state is established for electrodes of certain geometries (e.g., planar and spherical). However, a steady state cannot be attained for an infinitely long cylindrical electrode. Spherical electrodes exhibit an especially simple flux pattern—the concentration gradient equals the bulk substance concentration, c^0 , multiplied by the sum of the reciprocals of δ and r , the first term corresponding to the transient state and the second to the steady state (see Eq. 2),

$$\left(\frac{\partial c(x,t)}{\partial x} \right)_{x=r} = c^0 \left[\frac{1}{\sqrt{\pi Dt}} + \frac{1}{r} \right] = c^0 \left[\frac{1}{\delta} + \frac{1}{r} \right] \quad (2)$$

The first term predominates at short times ($\delta \ll r$), while the second at a sufficiently long time ($\delta \gg r$).

It can be seen that the time required to attain a steady state strongly depends on the electrode dimensions. That is, the smaller the electrode, the shorter the time. More precisely, this time is proportional to r squared, that is, to the electrode surface area (Table 1). If the time elapsed does not exceed that given in the first column of Table 1, then the contribution of the steady-state current to the overall current does not exceed 10%. At the time values corresponding to the second column, the contributions of the non-steady-state and steady-state currents are equal and at those corresponding to the third column the steady-state component amounts to 90%.

Table 1 Times, $t_{\delta/r}$, to attain definite δ/r ratios for different electrode radii. [$D = (25/\pi) \times 10^{-10} \text{ m}^2/\text{s} \approx 8 \times 10^{-10} \text{ m}^2/\text{s}$].

| r/m | $t_{0.1}/\text{s}$ | $t_{1.0}/\text{s}$ | t_{10}/s |
|--------------|--------------------|--------------------|-------------------|
| 0.001 | 4.0 | 400.0 | 4×10^4 |
| 0.000 1 | 0.04 | 4.0 | 400.0 |
| 0.000 01 | 4×10^{-4} | 0.04 | 4.0 |
| 0.000 001 | 4×10^{-6} | 4×10^{-4} | 0.04 |

The δ/r values in Table 1 apply to an ideally spherical electrode, but corrections can be made for some other electrode shapes [16–18].

2.1.2 Microelectrode arrays

Three principal cases can be distinguished when considering the diffusional flux toward a microelectrode array [19,20]:

- The gaps between the electrodes are wide compared to the diffusion layer thickness. Thus, the diffusion layers of the individual electrodes do not overlap. This separation of diffusion layers occurs for $\delta < W/2$, where the total width is $W = W_e + W_g$, W_e being the electrode width equivalent to $2r$ (see Section 2.1.1) and W_g being the gap width. The electrodes then do not affect one another and the overall current measured is the sum of the currents passing through the individual electrodes.
- If $\delta > W/2$, then the diffusion layers of the individual electrodes, A and B, partially overlap (Fig. 2). The angle ψ represents the degree of overlap. The overall current is then smaller than the sum of the currents passing through the electrodes when they operate independently.
- For the value $\psi = \pi/2$ (i.e., when $\delta \gg W/2$), the diffusion layers totally overlap so that the array behaves as a continuous electrode having the surface area equal to that of the whole array. Under these conditions, the signal is proportional to the surface area of the whole array, while noise is proportional only to the area of the electrodes. Thus, the signal-to-noise ratio is greatly improved.

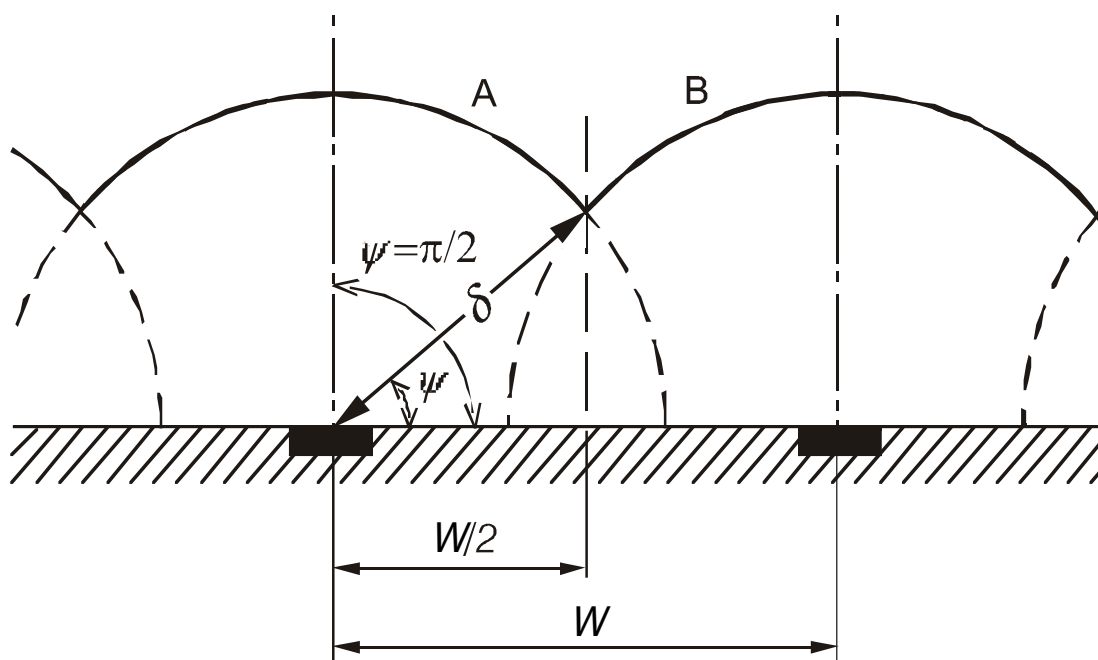


Fig. 2 Diffusion layer overlapping at closely spaced microelectrodes. For description, see the text.

The extent of the diffusion layer overlap can be expressed in terms of the overlap factor derived from the ratio of the overall current to the sum of the currents at the independent individual electrodes [21]. The value of the overlap factor depends on the electrode geometry and the time of electrolysis.

2.2 Consequences of the properties of microelectrodes

The principal consequences of the properties of microelectrodes are as follows:

- A steady state for a faradaic process is attained very rapidly (cf. Table 1).
- The faradaic-to-charging current ratio, I_F/I_C , is improved, as the charging current decreases in proportion to decreasing area of the electrode, while the steady-state faradaic current is proportional to its characteristic dimension. Therefore, the I_F/I_C ratio increases with the reciprocal of the characteristic dimension.
- The ohmic drop of potential, IR , is decreased as the measured currents are very low.
- The applied potential can be scanned very rapidly because the charging current is suppressed.
- The signal-to-noise ratio is greatly improved when an individual microelectrode performs under steady-state conditions or when the diffusion layers totally overlap in an array of microelectrodes.
- With microelectrode arrays used for measurements in flowing liquids, the amperometric signal (i.e., the current intensity) is enhanced not only through the above effects, but also by replenishment of the electroactive substance in the diffusion layer during the solution passage over the gaps between the electrodes [22].
- Interactions between the individual electrodes in the microelectrode arrays permit regeneration of the electroactive substance through redox cycling and derivatization of substrates to obtain products of desired properties.
- Small size of the electrodes permits measurements on very limited solution volumes.

2.3 Operational definition of microelectrode

It can be seen that no clear-cut boundary separates microelectrodes from classical electrodes used in electroanalytical chemistry. In order to attain the features characteristic of microelectrodes, as discussed above, not only the electrode size and shape must be considered, but also a kinetic parameter of the electroanalytical technique employed that governs the thickness of the diffusion layer developed (e.g., the potential scan rate for cyclic voltammetry) [23]. Relatively large electrodes ($2r \approx 10^{-4}$ m) may, under certain conditions, respond like a microelectrode, whereas under different circumstances the electrode must be substantially smaller ($2r \approx 10^{-6}$ m). Therefore, a definition specifying a certain geometric dimension is rather arbitrary and the following operational definition is recommended:

Microelectrode is any electrode whose characteristic dimension is, **under the given experimental conditions**, comparable to or smaller than the diffusion layer thickness, δ . Under these conditions, a steady state or a pseudo steady state (cylindrical electrodes) is attained.

3. PREPARATION AND ANALYTICAL APPLICATION OF MICROELECTRODES

3.1 Preparation

Microelectrodes and their arrays are usually prepared in the laboratory for a given purpose. The preparation procedures are not complicated but require very careful work and experience. There are several basic approaches to this task:

- Microcylindrical electrodes are obtained by sealing thin metal wires or carbon fibers in tapered glass capillaries (e.g., micropipettes). The protruding wire or fiber is then cut to the required length (usually less than 1 mm). There are high demands on the quality of the seal which must be tight,

without entrapped air bubbles. Epoxy resins that are most often used for sealing must be carefully selected to be sufficiently chemically resistant and noncontaminating.

- Microdisks are mostly prepared by fixing thin metal wires or carbon fibers in tapered glass capillaries by carefully melting the glass. The disk is then obtained by cutting off the protruding wire or fiber flush with the surface and thorough polishing of the surface to a mirror-like finish. The quality of the seal and of the polishing is decisive for obtaining a good quality microelectrode.
- Band electrodes can be prepared by sealing thin metal films into a suitable insulator. However, photolithographic techniques are more versatile and permit the preparation of electrodes with a broad range of shapes and sizes, both single electrodes and the electrode arrays.
- Mercury microelectrodes can be obtained by using a miniaturized hanging mercury drop electrode (spherical electrodes), or by electrolytically depositing mercury on a planar (usually disk) metal or carbon microelectrode (film or hemispherical electrodes). To obtain uniform and stable electrodes, metal supports are preferable. However, undesirable intermetallic compounds may be formed; this tendency increases in the order: iridium < platinum < gold < silver. The intermetallic compounds, produced by dissolution of the support material in mercury, alter the electrochemical properties of mercury electrodes [24]. Mercury microelectrodes prepared on carbon supports tend to be less uniform (formation of tiny droplets of mercury on the support surface) and exhibit poorer stability than those on metal supports.
- Microelectrode arrays are prepared in a very simple way by dispersing sufficiently small particles of a conductive material (usually a very fine graphite powder) in an insulator (paste electrodes with nujol or another pasting liquid, composite electrodes with various plastic matrices). Of course, these arrays are poorly defined electrochemically. Well-defined arrays are now almost exclusively prepared by photolithography.
- A promising approach to the preparation of microelectrode arrays involves passivation of a metal electrode surface with a monomolecular, nonconductive Langmuir–Blodgett film and formation of conductive channels in the film by uniformly dispersing in it molecules of a suitable substance. Single-molecule electron and ion gate sites are thus obtained forming a random array [25]. This approach is, however, still waiting for wider practical application.
- Like all solid electrodes, microelectrodes require suitable pretreatment and activation prior to measurements. The first step always involves the obtaining of a smooth surface (usually by mechanical polishing), followed by chemical or electrochemical conditioning, or by combination of the two. The most common procedure is electrochemical activation by potential cycling within a suitable range and in a suitable simple (mostly inorganic) electrolyte [26].

3.2 Applications

The applications of microelectrodes and microelectrode arrays are based on their typical characteristics listed above. They can be roughly divided into the following fields:

- *Electrochemical reaction mechanisms and kinetics.* The study of reaction mechanisms makes primary use of the decreased resistance and capacitance at microelectrodes permitting the use of various voltammetric techniques with very fast potential scans (up to ca. 10^6 V/s), measurement in a steady state and application of a great variety of solvents and supporting electrolytes including solvents of low relative permittivity values or samples without a supporting electrolyte added. Ac admittance measurement with microelectrodes is also very useful for the purpose [27]. It is then possible to follow rapid electrode processes as well as chemical reactions accompanying electrode charge transfer that involve unstable reactants and/or products. Reference electrodes with a high resistance can be used, which permits optimization of the reference electrode design from the point of view of suppression of the liquid-junction potential and contamination of the test solution with the reference electrode electrolyte (e.g., the use of double-junction electrodes).

- *Trace electrochemical analysis.* Trace analysis primarily utilizes the improved I_F/I_C ratio, leading to an improvement in the limits of determination. The wide range of solvents available also extends the applicability in trace analysis. The small IR drop sometimes permits measurement on samples of small salt concentrations (e.g., natural waters) or without supporting electrolytes; this not only improves the reliability of determinations, but also greatly facilitates speciation.
- *Electrochemical reactions in solutions of very high resistance.* In the absence or at a very low concentration of a supporting electrolyte, electrochemical investigations can be performed on systems of high resistance, such as undiluted organic liquid compounds and organic solvents in particular, poly(electrolytes) or colloids.
- *Analytical sensing.* Many sensors for gaseous substances employ microelectrode systems with liquid or solid-polymer electrolytes (e.g., sensors for monitoring of hydrogen, nitrogen oxides, sulfur dioxide, ammonia, and many others). The main advantage of microelectrodes here are small dimensions which also permit construction of multisensor arrays. The rapid charging and establishing of a steady state improve the sensor response rate.
- *In vivo measurements on biological objects.* Microelectrodes are very well suited for monitoring of important compounds in the cells of living organisms; simultaneous determination of ascorbic acid and dopamine may serve as a typical example. Here, a small size of the electrode is essential. The selectivity of measurement can be adjusted, to a certain extent, by a suitable pretreatment of the electrode surface [28].
- *Detection in flowing liquids.* Flow detection is a very wide area involving continuous monitoring of substances in streams of liquids, continuous flow and flow injection determinations and, most important, detection in high-performance liquid chromatography (HPLC) and capillary electrophoresis (CE) [22]. In order to avoid peak broadening due to detection, effective volume of a detection cell should not be larger than the volume of one theoretical plate characterizing the separation system. Therefore, microelectrodes are indispensable for detection in the capillary separation systems. The use of rapid potential scan voltammetry permits separation in two domains (time and potential) which is analogous to diode array spectrometric detection and greatly facilitates identification of the analytes. Microelectrode arrays enhance the measuring sensitivity due to replenishment of the diffusion layer during the solution passage over the gaps between the electrodes and improve the selectivity and reliability of the measurement because the array differentiates, to a certain degree, between reactions controlled by mass transport and those controlled by the charge transfer. Pairs of microelectrodes can be used as a generator and a collector electrode to improve the detection sensitivity and selectivity. A future possibility is construction of multichannel detectors with a certain number of microelectrodes individually polarized to different potentials.
- *Scanning electrochemical microscopy (SECM).* The SECM techniques are becoming an increasingly important area of microelectrode application for imaging redox centers present in thin solid films [29,30].

In addition, there are other specialized uses of microelectrodes and their arrays, such as the use of interdigitated microelectrode arrays, coated with redox or π -electron conductive polymers, to study the transport of electrons and ions in these polymers. These charge transport systems can be potentially employed for construction of electrochemical devices for current rectification, charge storage and amplification, electron-hole pair separation, and for creating gates for ion flow [31].

4. FUTURE TRENDS

A continuing development of microelectrode systems can be expected, especially in the following areas:

- An improvement in the microelectrode fabrication, with an emphasis on microelectronics technologies.

- An improvement in the construction of multipotentiostat circuitry permitting construction of efficient multichannel cells with individually addressed working electrodes for application to the HPLC and CE detection and to trace analyses of complex samples employing chemometric procedures.
- Further sensor development, especially multichannel sensors.

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