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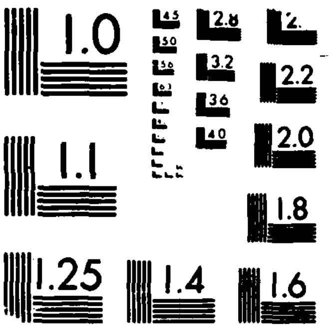

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Instrumental Configurations and Electrode Design for Voltammetry in Very Dilute Solutions employing Carbon, Gold and Platinum Microdisk Electrodes in Static and Flow through Cells

By

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INSTRUMENTAL CONFIGURATIONS AND ELECTRODE DESIGN FOR VOLTAMMETRY IN VERY DILUTE SOLUTIONS EMPLOYING CARBON, GOLD AND PLATINUM MICRODISK ELECTRODES IN STATIC AND FLOW THROUGH CELLS

#74

Analytica Chimica Acta

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ABSTRACT

Microelectrodes are predicted to provide greater analytical sensitivity than conventional-size electrodes. In this work, convenient methods of preparing platinum, gold and carbon fibre microdisk electrodes in stationary and flowing solution configurations are presented and instrumental requirements for measurement of current-voltage curves with low concentrations assessed. The detection of micromolar or lower concentrations with microdisk electrodes requires measurement of femtoamp currents and is outside the range of most commercially available instrumentation. Fortunately, the ohmic (iR) drop with microelectrodes is very small and reference electrode polarization is unimportant so that a two electrode format without a potentiostat can be employed. The use of a microprocessor-based function generator and data storage system, in conjunction with a picoammeter or femtoammeter therefore provides inexpensive, versatile and very sensitive electrochemical instrumentation for voltammetric detection in very dilute solutions. Unfortunately, instrumentation incorporating a picoammeter or femtoammeter is limited by the relatively slow rise time and this places restrictions on scan rates in all voltammetric techniques and on pulse widths in transient techniques such as differential pulse and square wave voltammetry. The novel use of a picoammeter as a current amplifier is reported which permits commercially available instrumentation to be used with microdisk electrodes.

INTRODUCTION

The use of microelectrodes has become an important area of research in electrochemistry in the last decade. Microcylinder and microdisk electrodes as well as arrays of microelectrodes have been designed, characterized and applied to a number of electrochemical applications (1-14). The advantages of microelectrodes over conventional-size electrodes for (i) minimizing (ohmic) iR drop distortions (particularly at high scan rates) (5,8,9), (ii) examining redox processes at very positive and very negative potentials (10), (iii) undertaking electrochemical measurements in the absence of added supporting electrolyte (11), (iv) electroformation of a single metal nucleus (12) and (v) electrochemical detection where microsensors are required (3,4,14,15) have been extolled. A disadvantage of microcylinder electrodes is that they cannot be polished reproducibly which prevents their widespread use in analytical applications. Conversely, microdisk electrodes are well suited for reliable and stable electrochemical detection purposes.

Theoretically, single microdisk electrodes have been shown to provide the potential for considerably greater analytical sensitivity than conventional-size electrodes (5), i.e. the ratio of faradaic to charging current is larger for microelectrodes than for conventional electrodes. The experimental exploitation of this enhancement is complicated by the difficulty of monitoring extremely small voltammetric currents (pico to femtoamperes) at low concentrations of electroactive species using sensors having small areas. The measurement of the pico- to femtoampere currents requires extremely sensitive instrumentation. None of the commerically available electrochemical analyzers provide this feature. Consequently, there has been a great deal of interest in using arrays of microelectrodes (7,15-17), i.e. multiple microelectrodes connected in parallel, which yield much higher currents without altering the desirable characteristics of single microelectrodes. This allows voltammetric techniques to be performed with commercial instruments. Such an ensemble of microelectrodes may further increase the analytical sensitivity when overlap of adjacent diffusion layers is present, as theoretically predicted by digital simulation (18). For instance, the sensitivity is predicted to be up to three orders of magnitude higher by use of pulsed wave forms with microelectrode arrays instead of conventional size electrodes. While the array electrodes can be employed in many applications, their physical size excludes their use where extremely small sensors are needed, such as in on-line detection for capillary separative techniques. Furthermore, arrays of microelectrodes are more difficult to polish reproducibly than single microdisk electrodes. This necessitates further development of voltammetric instrumentation for single microelectrodes. In particular, investigations for the proper measurement of extremely small voltammetric currents are to be pursued.

Noise levels are undesirably high when measuring subnanoampere currents using potentiostatic control provided by commercial instruments. Wightman and co-workers modified three electrode potentiostats of conventional design for sub pA current measurements with time constants of 10 ms (3,15) and 100 ms (7) respectively permitting the detection of 10^{-7} $\underline{M}$ analyte (3) concentrations. The very small currents at microelectrodes, however, eliminate the need for a potentiostat so that electrochemical experiments may be performed conveniently with a simple two electrode system incorporating a wave function generator and a picoammeter or femtoammeter (4,11,12,19). In this paper, the advantages and disadvantages of various instrumental and electrode configurations employing single microdisk electrodes in micromolar analytes, yielding subpicoampere currents are described. The use of a picoammeter as a current preamplifier for commercially available instrumentation is reported. Methods for simple construction of platinum, gold and carbon fibre disk electrodes with radii 1 to 25 µm are also discussed. Both stationary and flow through cell configurations are considered.

EXPERIMENTAL

All electrochemical experiments were performed with either a 2 or 3 electrode system enclosed in a solid aluminium Faraday cage. A variety of instrumental configurations were employed. Conventional instruments used were an EG & G Princeton Applied Research (PAR) 174A Polarographic Analyzer, a Metrohm VA Detector Model E611 with a Metrohm Scanner Model E612 and a BAS 100 Electrochemical Analyzer (Bioanalytical Systems). Other instrumentation was constructed from function generators, current measuring devices and recording units. Function generators used were a PAR 175 Universal Programmer, a Metrohm VA-Scanner Model E612 or a Motorola D2 Kit[20]. A Keithley 480 Picoammeter or a Keithley 614 Electrometer in the current mode, the latter enables femtoamp currents to be measured, were used as current sensors in the two electrode format. Plots of data were recorded on a Houston Instruments Omnigraphic 2000 Recorder for scan rates < 500 mV/s or a Tektronix Model 5103 N Dual Bean Storage Oscilloscope in conjunction with a Tektronix C-5 Oscilloscope Camera for scan rates > 500 mV/s. Outputs from the BAS 100 were recorded using a Houston Instrument HIPLOT DMP-40 Plotter. The D2 Kit was interfaced directly into a Sphere Computer (Paris Electronics, Sydney) and subsequently to a DEC 20/50 computer, if required[21] thereby enabling data storage, data evaluation and background correction to be made. Flow-through cell applications were tested using a BAS LC-6 pump, a Rheodyne 7125 injector and Metrohm EA 1096 wall-jet cell in a flow-injection mode.

The Keithley 480 Picoammeter was also used as current amplifier to the BAS 100 Analyzer or the Metrohm VA Detector. An illustration of how a picoammeter can be used as a preamplifier for enhanced sensitivity is illustrated by the following considerations which apply to the Metrohm detector. The working electrode is connected to the input of the Keithley 480 picoammeter, the high analog output is connected to the working electrode input of the Metrohm 611 potentiostat and the low output of the picoammeter is connected to the potentiostat shield. Since the full-scale output of the picoammeter is one volt across 1000 ohms on all ranges, the low impedance input stage of the potentiostat "sees" an apparent cell current of 0-1 mA. For example, an actual cell current of 5 pA produces a full-scale current output signal from the potentiostat when the picoammeter is set on the 1 nA range and the potentiostat is set on the 5 µA range. This is in contrast to the 0.1% of full-scale current output that would be seen for the same cell current using only the potentiostat at its most sensitive (5 nA full-scale) range. Similar considerations can be stated for the same picoammeter as preamplifier to the BAS 100 Analyzer.

A Ag/Ag^+ (0.1 $\underline{M}$ $AgNO_3$ (CH_3CN), a Ag/AgCl (aqueous 3 $\underline{M}$ NaCl) or a platinum wire were used as reference electrodes for data obtained in acetonitrile for the oxidation of Ferrocene (Fc) according to:

$$\mathrm{Fc} \qquad \mathrm{Fc}^{+} + e \tag{1}$$

In the case of a three electrode assembly, a Pt wire was used as the auxiliary electrode. Two electrode configurations with either the PAR 174A or BAS 100 instruments rather than the standard 3-electrode mode was achieved by connecting both the auxiliary and reference leads to the reference electrode.

A range of platinum and gold microelectrodes used in this work were prepared at Southampton University as described in the literature[11,13]. These electrodes are mounted in all-glass assemblies. Alternative and simpler construction methods involve sealing metal wires or carbon fibres in glass or epoxy contained in a glass tube to produce the microelectrodes shown in Figure 1. 50 µm to 10 µm diameter 99.9% platinum or 5 µm to 1 µm diameter Wollaston wires (99.9% platinum coated with a Ag layer) were purchased from Goodfellow Metals (Cambridge, England). Carbon fibres were obtained from Hercules Corporation (Magna, Utah, U.S.A.). Construction methods for microelectrodes in both stationary and flow through cell configuration are discussed separately. Microelectrodes were cleaned and polished before each experiment as described previously[11,19]. HPLC Grade acetonitrile, AR grade ferrocene, and electrochemical grade tetraethylammonium perchlorate were used as received. For those experiments requiring dry acetonitrile, the solutions were dried in situ by adding neutral alumina[11,22] (Brockman Activity 1, predried at 200°C) to the cell.

Fabrication of Microelectrodes for a Stationary Cell Configuration

(i) Epoxy-Sealed Microelectrodes

A 2 ml volumetric pipette (Fortuna W.G. Co., soda glass) was cut through the center of the bulb. The narrow ends were fused and drawn out in such a way that the thickness of the glass (~ 0.7 mm) was retained and the outer diameter was ~ 2 mm at the thinnest point. Cutting at the thinnest point provided two glass holders for microelectrodes (Fig. 1a). A small hole was blown 1.5 cm from the bottom tip and acted as the inlet for introduction of the sealing resin. The platinum electrode wire (~ 15 mm) was soldered to a copper wire and inserted into the tube such that it just protruded. The sealing resin was injected carefully into the tube using a plastic syringe until the resin first appeared at the tip of the electrode. Araldite (Super Strength Araldite, Ciba-Geigy Australia Ltd.) or Torr Seal (Varian Associates, Palo Alto, CA) were used as the resins. The thickness of the epoxy seal should be < 0.5 mm, otherwise reproducible polishing is difficult. A coaxial cable was connected to the copper wire and was sealed into the top of the electrode using heat-shrink sleaving (irradiated polyolefin).

After a curing period of at least 24 hr., the tip was ground flush using a rotating diamond disk. It was then polished by hand on wet and dry emery paper, starting with B500 and working down in steps to P1200. Finally, it was polished with alumina (1 µm) water slurries and commercial metal polish (Brasso, household quality) on a polishing cloth.

Construction of a 2.5 µm radius (platinum) electrodes using Wollaston wire was achieved via a modified method. After soldering the Wollaston wire to the copper support, the Pt electrode was passed through the tip of glass solder such that 10 mm of the Wollaston wire protruded. A gentle flow of air was passed down through the tube to prevent corrosive vapors dissolving the tin solder, and the Ag coating was removed from the bottom 5 mm of wire as described in reference 5. As an alternative to protecting the solder joint by a flow of air, it may be covered with Torr Seal during the etching stage. The wire is then sealed into the tube as described above. The construction of the epoxy-sealed platinum microelectxrodes is illustrated in Figure 1a.

Carbon fibre microelectrodes were prepared in a similar manner as the platinum microelectrodes except the fibre and copper support were connected using silver epoxy (RS Components Ltd., No. 555673). This connection is illustrated in Figure 1b.

(ii) Glass-Sealed Microelectrodes

Glass-sealed microdisk electrodes were prepared using the same glass support as the epoxy-sealed microelectrodes (Fig. 1c). The platinum electrode was allowed to protrude from the tip of the tube by a few mm. After temporarily sealing the hole in the side of the glass tube, the top of the tubing was connected to a vacuum (water aspirator), and the wire was sealed into the remainder of the thin tip by very gently heating from the bottom up to the top of the thin section using a narrow bore oxy-acetylene torch. When the sealing procedure was complete, Araldite was injected into the remainder of the electrode in order to act as a solid support for the wire. This construction procedure was more difficult for the smaller (Wollaston wire) microelectrodes than using the epoxy-seal method.

Fabrication of Microelectrodes in Flow Through Cell Configuration

Two micro-disk electrodes were prepared to fit the working electrode port of a Metrohm EA 1096 wall-jet type flow-through detector cell. The cell design required that the disk be located at the centre of the flat end face of a 7 mm o.d. insulating rod. One microsensor was made by fusing glass around a 50 μm diameter platinum wire. The second was prepared by sealing a 5 μm diameter Magnamite carbon fibre (Hercules Corp.) into a glass capillary tube with Torr Seal. Detailed instructions for the preparation of these electrodes will be given in a subsequent paper.

RESULTS AND DISCUSSION

(a) Instrumental Configurations

The electrochemistry of the Fc/Fc$^+$ couple in acetonitrile at platinum, gold and carbon fibre microdisk electrodes with radii from 0.5 to 30 µm has been examined using a number of instrumental configurations and experimental conditions. It has been found that the best instrumental configuration will depend on the type of electrochemical measurements that are being made. We examined each system in terms of sensitivity, voltage range, scan rate range and versatility.

The three electrode format which has previously been considered as mandatory for most voltammetric electrochemical experiments is not universally optimal when using microelectrodes. Generally, the currents produced by electroactive species in submillimolar concentrations are so small that they cannot be detected by most commercially available instruments. Several options were available to achieve a two electrode format with an ability to measure picoamp or femtoamp currents. Firstly, a conventional electrochemical system was used (BAS 100, Metrohm VA Detector), except the current was preamplified by a picoammeter and the reference and the counter electrode connections were both attached to the reference electrode of the two electrode configuration. Alternatively, electrochemistry is conveniently performed by use of a picoammeter or a femtoammeter with a function generator in a two electrode system, Figs. 2 and 3 show examples of the detection of micromolar concentrations of electroactive species in stationary (Fig. 2) and flow through (Fig. 3) cell configurations. In these and all subsequent figures the raw data are presented without background correction on the stated instrumentation. The cyclic voltammetric data depicted in Fig. 2 were obtained with the picoammeter as preamplifier to the BAS 100 Electrochemical

Analyzer using a 0.5 µm radius platinum microdisk electrode. This experiment was performed without any deliberately added supporting electrolyte and with an analyte concentration of 6.6 µM. The results indicate a detection limit of about 2 pA under linear sweep conditions without background substraction and if the picoammeter is used as preamplifier to the BAS 100 and is considerably lower if used as a pre-amplifier in the Metrohm 611 instrument. Note that this experiment is not possible using a single commercial instrument.

Fig. 3 is illustrative of the flow-injection signals obtained with microdisk electrodes in a wall-jet flow cell and highlights the new aspects which need to be considered in this area. Fig. 3a actually shows the sensitivity limit of the larger 50 µm platinum electrode when the Metrohm 611 detector is used without preamplification. This detection level is of little utility with the smaller carbon disk, since its area, and hence the current, is about a factor of 25 smaller than for the platinum disk. However, Fig. 3b shows that excellent sensitivity is obtained with the smaller electrode when the picoammeter is used as preamplifier. A detailed presentation of the behavior of these and other microelectrodes in the wall-jet flow through configuration will be given in a subsequent paper.

Two-electrode operation with current preamplification using the picoammeter provide a current detection limit increase of about two orders of magnitude compared to the sensitivity of the commercial instruments. The most versatile and powerful instrumental combination, however, is a versatile function generator, such as one based on the D1 microprocessor Kit (20,21) or equivalent system (23), coupled to a picoammeter or a femtoammeter (Fig. 4). Such a configuration enables all electrochemical techniques including pulse and AC methods to be utilized with extremely high sensitivity, provided the time constant of the current measuring device is appropriate compared to the time scale of the experiment.

While the use of a picoammeter or femtoammeter greatly increases the sensitivity of detection, the Keithley instruments employed in this work have a relatively slow response time. For example, the scan rates which can be applied in cyclic voltammetry are limited to less than 500 mV/s when the picoammeter is introduced into the circuit. The Keithley 614 electrometer only allows sweep rates < 50 mV/s to be employed. Similar considerations apply when using differential pulse and related techniques. Fig. 5 shows the differential pulse and square wave voltammograms for oxidation of 1 mM Fc in acetonitrile using the Motorola D2 "Kit" as the wave generator and data acquisition system together with the picoammeter in a two electrode format. A long pulse width (> 60 ms) and a slow sweep rate (< 30 mV/s) are essential when the picoammeter is incorporated and large amplitudes are used. The limiting values with the Keithley 614 Electrometer are about an order of magnitude larger for the pulse width and smaller for the scan rate respectively than those for the picoammeter. Similar restrictions were reported for the three electrode potentiostats modified for low current measurements (3,15).

The detection of trace amounts of analytes using microelectrodes yields currents in the picoampere to femtoampere range. With the technology described in this work, measurements must be restricted to slow scan rate, low frequency or long pulse width methods. In summary, a versatile function generator coupled to a picoammeter or femtoammeter with fast response using a two electrode format would appear to provide the most useful instrumental arrangement for electrochemical detection with microelectrodes (Fig. 4). Under steady state conditions, detection limits in the nM range are thereby predicted to be accessible even in non-aqueous solvents such as acetonitrile. Practical examples are being examined in these laboratories and will be described in due course.

(b) Performance of microdisk electrodes

The goal in most electroanalytical applications is to measure the concentration of electroactive species by the monitored current and to identify the component via half wave potential. This requires that the electrodes retain constant properties throughout the experiment which can be experimentally assessed by repetitive cyclic voltammetry. Construction principles of microdisk electrodes encompass the sealing of a metal wire or a carbon fibre with glass or with epoxy resin confined in a glass tube (see Fig. 1). The sealing with epoxy resin is a relatively simple, cheap and convenient method. Electrodes having radii down to 2.5 µm have been successfully prepared in this manner in our laboratory and elsewhere (2-4). In general all glass electrodes are superior with respect to analytical performance. It was found that both the magnitude and the shape of the response in successive cycles can degrade quite substantially with epoxy sealed electrodes if epoxy layers of about 0.5 mm thickness are employed (Fig. 6). Only minor changes of the limiting current and the half wave potential were observed for glass sealed microdisks. A carefully applied epoxy seal gives equivalent results provided the thickness of the insulating epoxy layer around the electrode is not much larger than the diameter of the microdisk.

CONCLUSIONS

For both dilute solutions of analytes and microdisk electrodes with radii < 10 µm, it seems that simple instrumentation consisting of a microprocessor based function generator/data acquisition system and a picoammeter or femtoammeter used in a two electrode format is to be preferred to the potentiostatic three electrode configuration. Commercially available picoammeters and femtoammeters are unfortunately characterized by large time constants (>> 1 ms) which restricts their use to slow scan rates, large pulse widths and low frequencies. Microelectrodes, however, yield voltammetric currents in the picoampere to femtoampere range and have unique properties in the micro to millisecond time domains. This calls for the design of new femtoampere (or even sub-femtoampere) current measuring devices with time constants much less than 1 ms.

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CAPTIONS FOR FIGURES

Figure 1

Simple construction principles of microdisk electrodes. (A) Epoxy sealed metal wire microelectrode; (B) Enlargement of epoxy sealed carbon fibre electrode; (C) Enlargement of glass sealed metal wire electrode. Denoted parts; 1 = coaxial cable; 2 = heat shrink sleeve; 3 = earth; 4 = solder; 5 = copper wire; 6 = glass support; 7 = epoxy resin; 8 = hole for injection of epoxy resin; 9 = metal wire; 10 = electrical connection with silver epoxy; 11 = carbon fibre; 12 = glass sealed tip.

Figure 2

Cyclic voltammograms at a 0.5 μm radius platinum microdisk electrodes for oxidation of 6.6 μM ferrocene in acetonitrile without any deliberately added supporting electrolyte. The scan rate was 5 mV/s. A two electrode instrumental configuration with picoammeter as preamplifier to the BAS 100 Electrochemical Analyzer was used.

Figure 3

Flow-injection peaks for ferrocene in acetonitrile with microdisk electrodes in a Metrohm EA1096 wall-jet cell in three electrode mode. Sample size and flow rate were 20 μl and 1.4 ml/min respectively. (A) 50 μm platinum microdisk electrode, 4 μM ferrocene in 0.01 TEAP, E = 1.1 V vs Ag/AgCl(3 M aq. NaCl), Metrohm 611 detector only. (B) 5 μm carbon fibre microdisk, 0.1 μM ferrocene in 1 mM TEAP, E = 1.0 V vs Ag/AgCl(3 M aq. NaCl), Metrohm 611 detector with picoammeter as preamplifier.

Figure 4

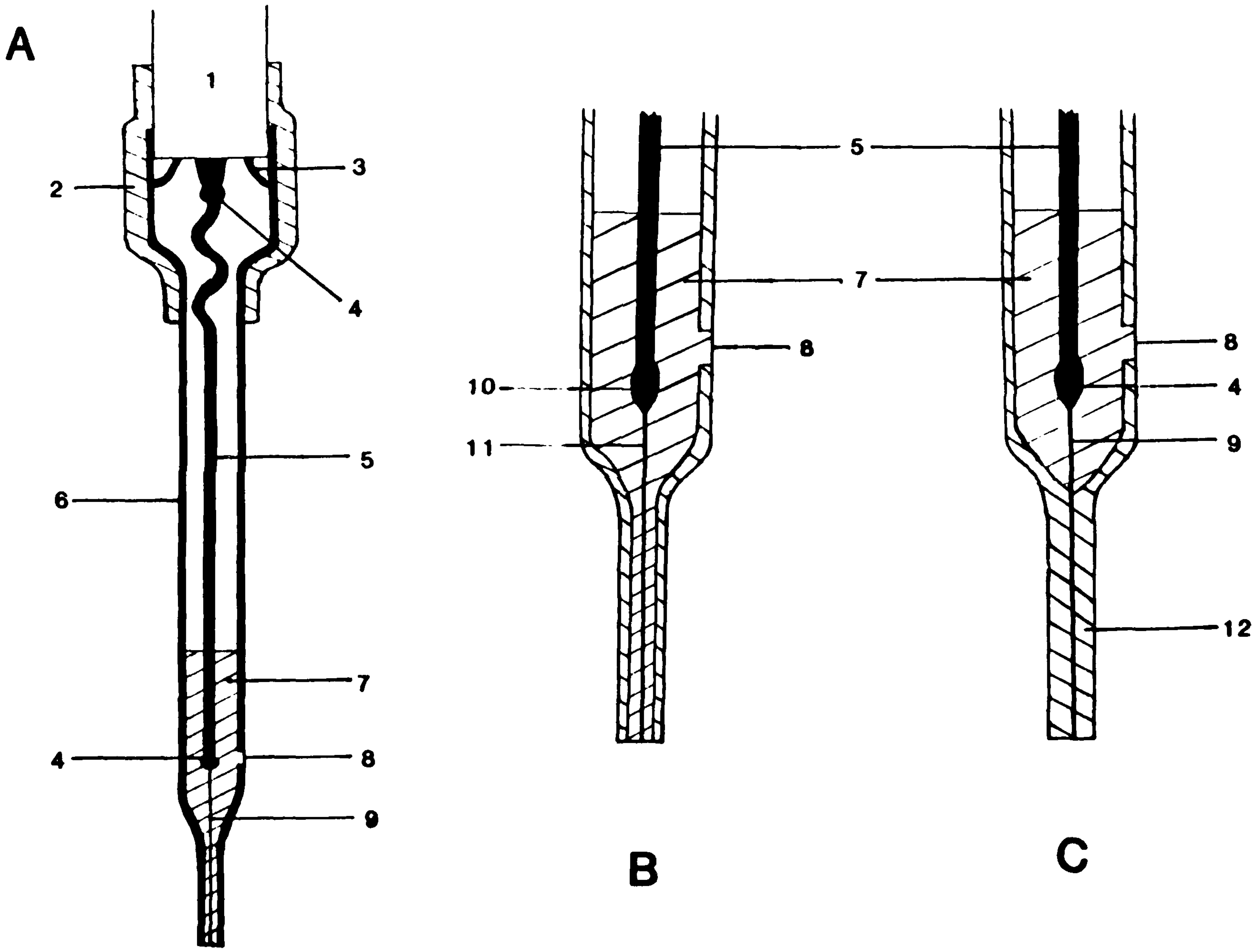
Block diagram for versatile microprocessor based instrumentation for measurement of low currents associated with microdisk electrodes.

Figure 5

Differential pulse (a) and square wave (b) voltammetric responses for oxidation of 1 mM ferrocene in acetonitrile (0.1 M TEAP) using the Motorola D2 Kit wave generator/data acquisition system and the Keithley 480 picoammeter in the two electrode format (Figure 4) with a 2.5 μm gold microdisk electrode. The pulse width, stair case ramp and amplitude applied were 100 ms, 5 mV and 50 mV respectively in both cases. The scan rates were 5.1 mV/s (a) and 25.0 mV/s (b).

Figure 6

Cyclic voltammograms for oxidation of 1 mM ferrocene in acetonitrile with 0.1 M TEAP with a 25 μm radius platinum microdisk embedded in epoxy resin. Both the response of a properly polished electrode (a) and the degradation in successive scans (b) is depicted. The scan rate was 5 mV/s.



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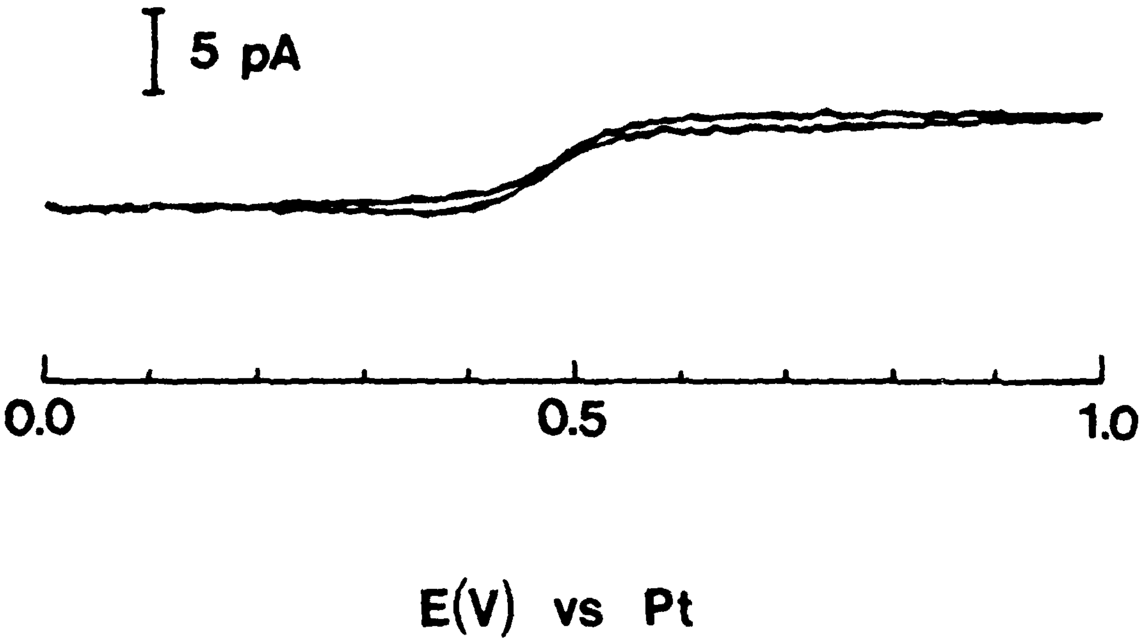
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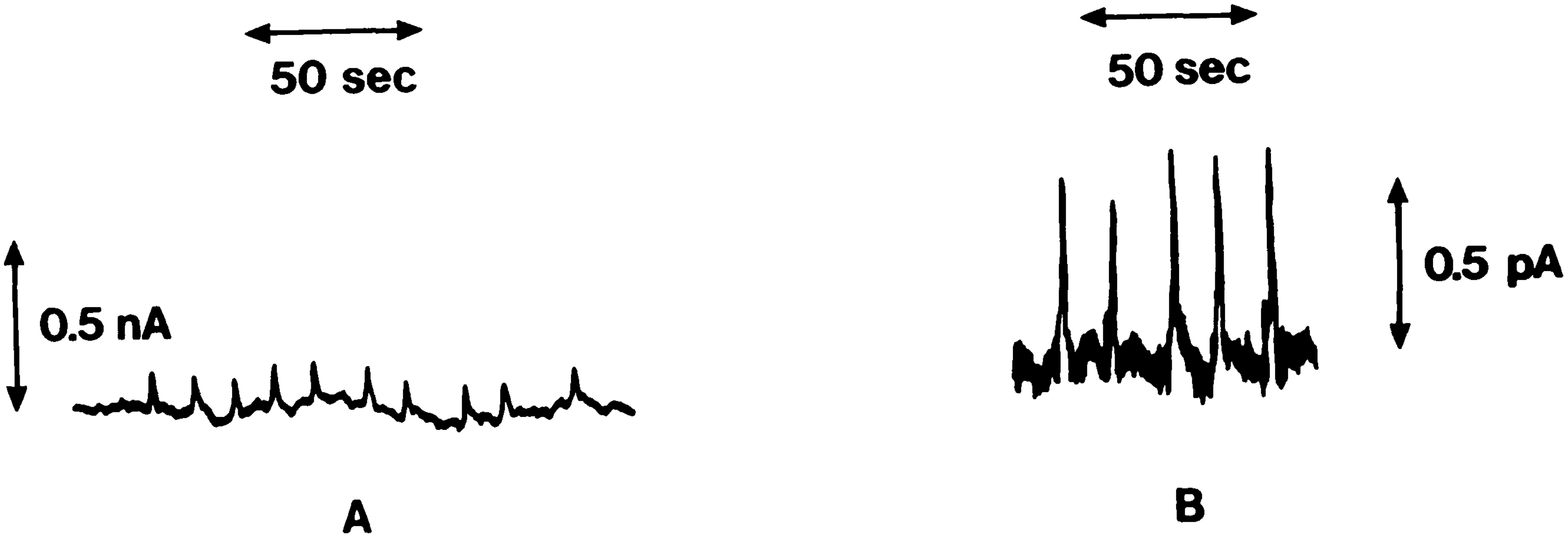
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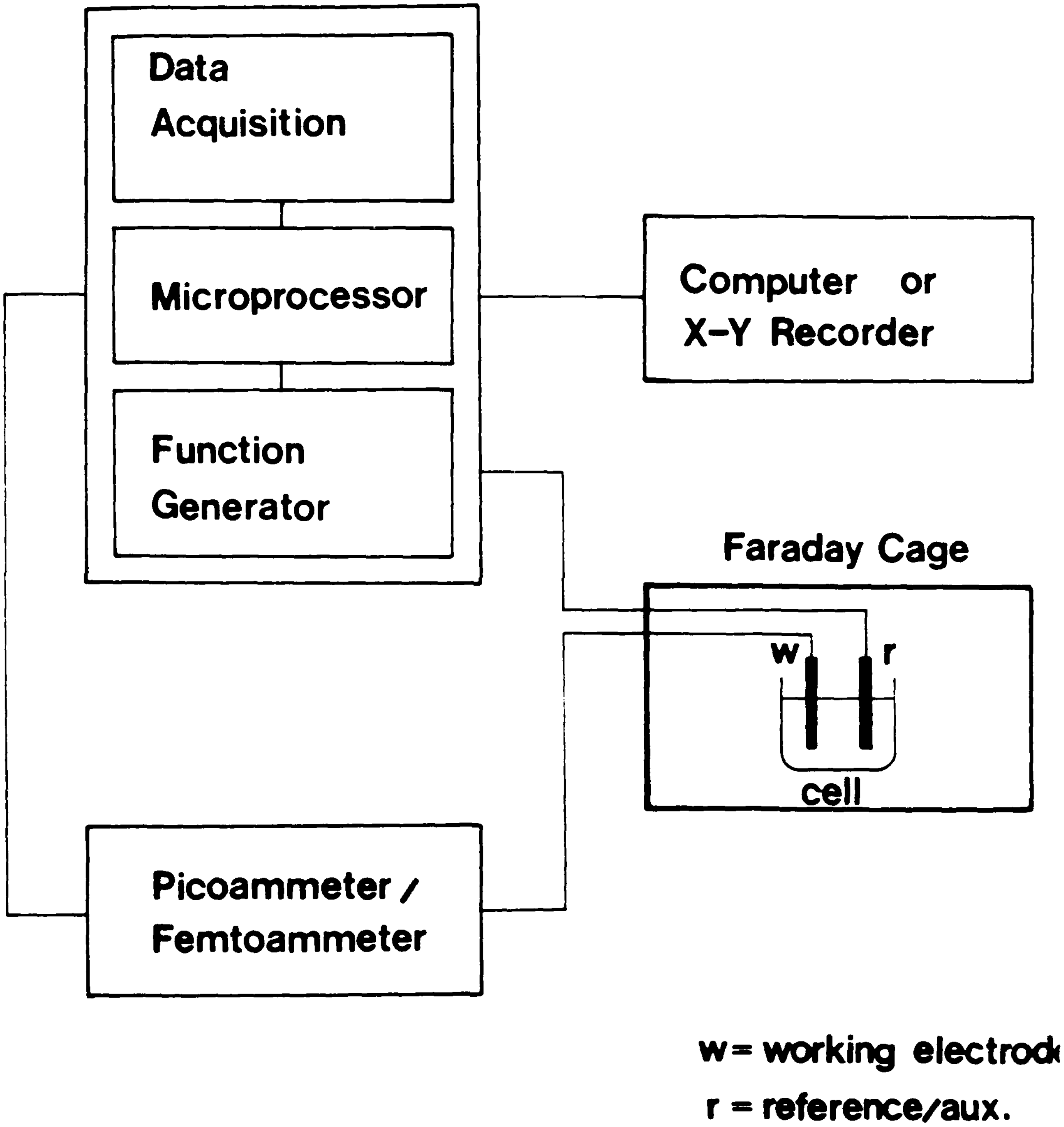
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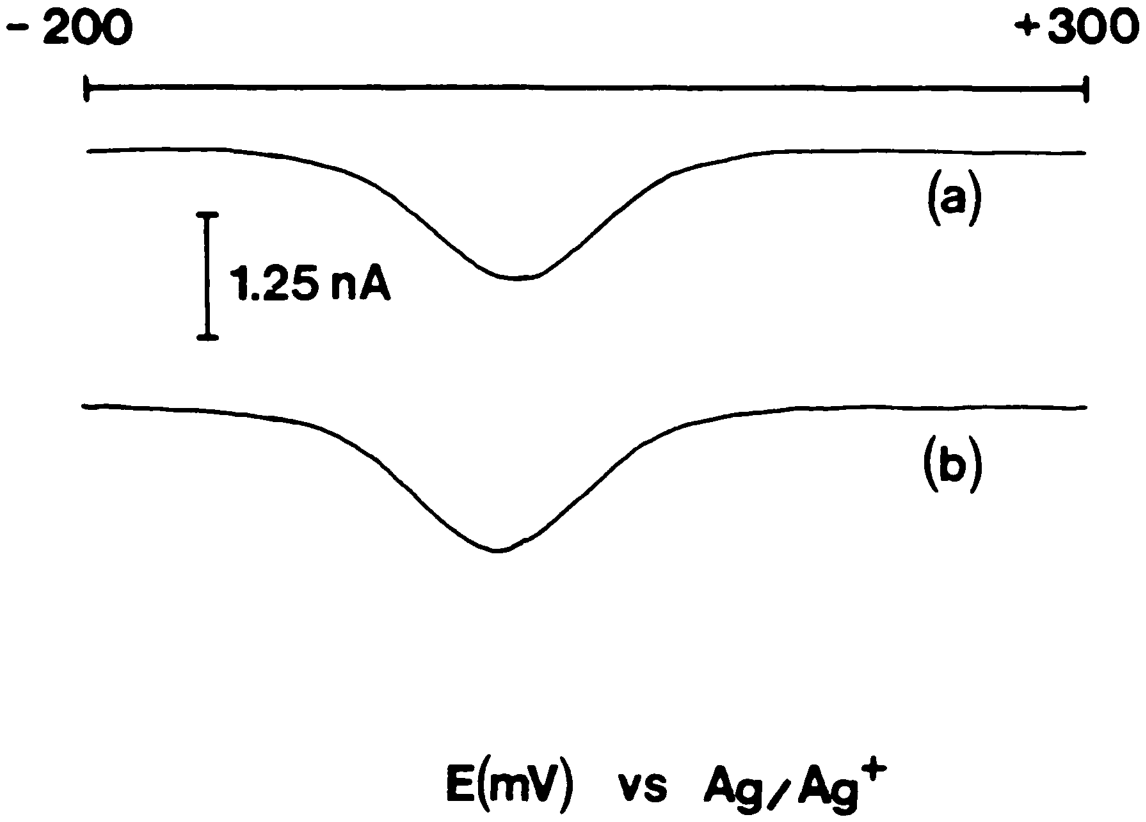

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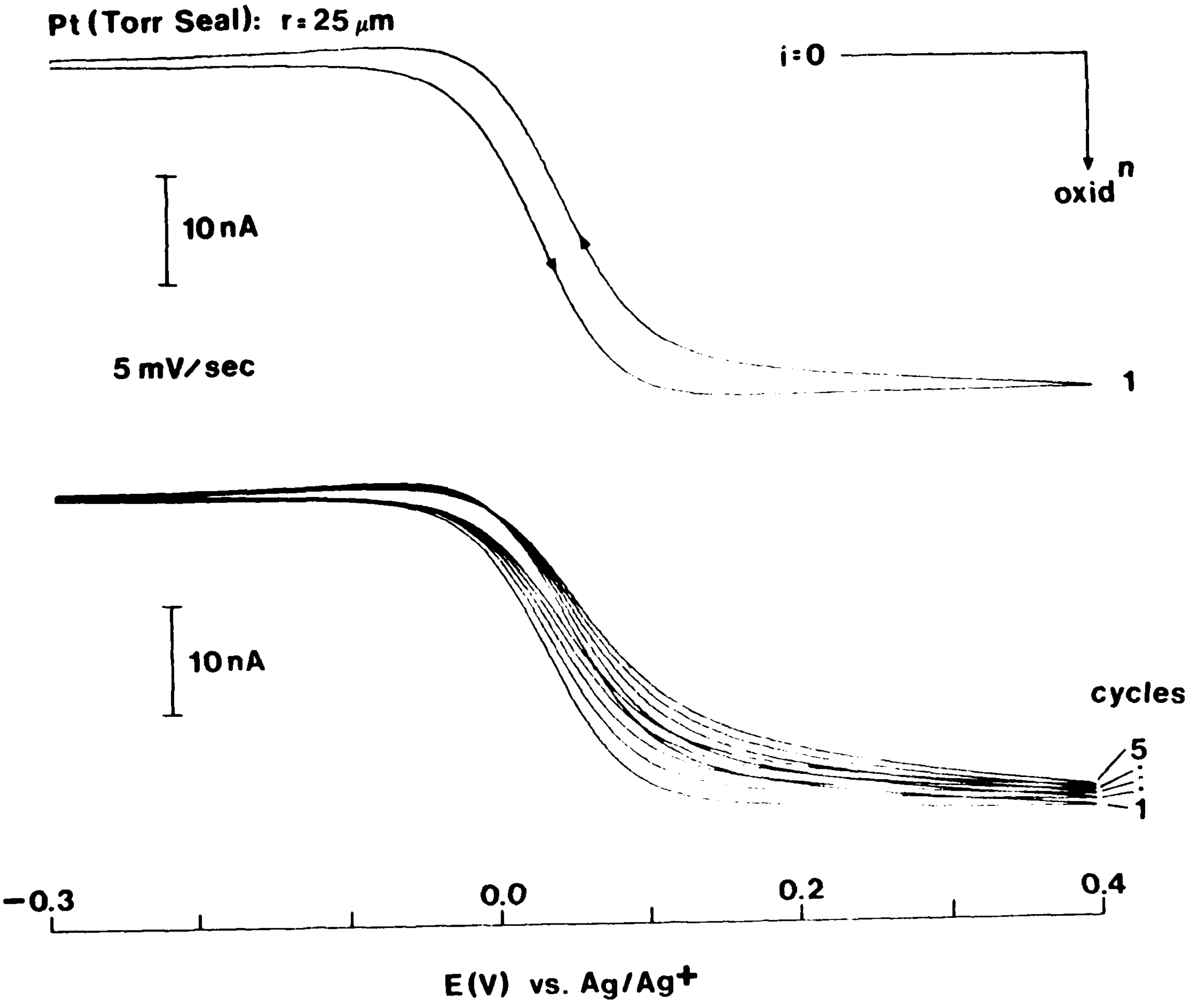
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oxid^n
10 nA
5 mV/sec
1
10 nA
cycles
5
1
−0.3
0.0
0.2
0.4
E(V) vs. Ag/Ag+

(b)

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