Computer-controlled instrumentation for fast voltammetry at ultramicroelectrodes

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In this article we describe an electrochemical experimental setup for cyclic voltammetry operating from low (1 V/s) to very high (200 kV/s) scan rates. The system is designed to achieve an acceptable cost and to be user friendly for nonexperts. The instrumentation is based on a commercial arbitrary wave form generator, a digital oscilloscope, a general purpose interface bus interface to a PC, and a laboratory-built potentiostat. There are no complicated manual operations, instead the software creates dialog with an operator to control commands for the instruments. Requirements for the wave form synthesis and the data acquisition are given. Various data-smoothing methods for treating 8-bit fast scan data are evaluated. The performance was tested on the oxidation of ferrocene in acetonitrile. The estimated value of the standard heterogeneous rate constant, $k^0 = 0.8 \pm 0.1 \, \mathrm{cm \, s^{-1}}$, is in reasonable agreement with the most recent reports from other laboratories. © *2000 American Institute of Physics.* [S0034-6748(00)00404-4]

I. INTRODUCTION

Electrochemical studies of very fast electron transfer reactions are often distorted by a high solution resistance R of a sample under investigation and consequently by a low time constant of an electrochemical cell. Progress has been made by following the notion that these effects may be minimized if the size of the working electrode is reduced to a radius of the order of micrometers.[1–5] The interfacial double layer capacity C decreases in proportion to the surface area, thus resulting in a shorter time constant RC of the cell. The faradic current, which is the current component of interest, observed on such electrodes is correspondingly smaller. However, a much faster relaxation process can also be investigated. Typical cyclic voltammetry experiments apply a triangular voltage wave form to an electrochemical cell. The reduction and oxidation currents are recorded during the forward and the reverse voltage scans which complete one voltammetric cycle. Ordinary compounds, with both redox states chemically stable, yield a pair of reduction and oxidation peaks. The absence of a current peak during the reverse scan often indicates that the reduction product is chemically decomposed into an electrochemically inactive compound. Any short-lived intermediates can be detected at a sufficiently higher scan rate, at which the decomposition rate plays a minor role, thus enabling a pair of reduction-oxidation peaks to be observed. To this end, the reverse scan must be faster than the rate of a coupled chemical reaction. The faster the slope of the voltage scans, the more shorter-lived intermediates can be detected. Conventional electrodes (with diameters of 1–10 mm) and electrochemical instruments impose a limit on the voltage scan rates of approximately 50 V/s. Experiments using ultramicroelectrodes extend the scan rates to approximately 100 kV/s, which enhances voltammetric methods. Fast measurements on electrodes of 1–100 μm require sophisticated instrumentation that guarantees distortion-free registration of low-level electrochemical currents in a noisy environment. This is a prerequisite for gaining the full advantage of a much shorter time constant of such electrode sensors. Several papers have dealt with the design of potentiostats[6–8] which are needed for an adequate fast electronic control of the applied potential. Also, the construction of ultramicroelectrodes involves a state-of-the-art technique that has been developed in several laboratories.[9] The source of a fast voltage scan and of a fast data acquisition system has tacitly been assumed to be a trivial matter. However, routine laboratory work often involves handling reactive samples of limited stability and therefore requires an easy and time-efficient adjustment of all instrument components by nonexperts.

In this article we describe a hardware/software approach for a low-cost solution to these problems. We will describe a system consisting of commercial instruments (an arbitrary function generator and a fast digital oscilloscope), a home-made potentiostat and the general purpose interfase bus (GPIB) interface for a computer controlled operation. The rules that the algorithm is based on will be described. Possible solutions to the problem of the 8-bit resolution of a fast storage oscilloscope will be evaluated. The voltammograms presented here show the performance of our system, how-

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ever, their electrochemical interpretation is not the main goal of this article.

II. INSTRUMENTS

The linear-scan voltage (to be applied to the working electrode via a potentiostat) was derived from a function generator model DG340 (Stanford Research Systems). This particular model features the upper frequency limit 15MHz and it not only provides the sine, square and triangular outputs, but also a user-defined arbitrary wave form. The arbitrary wave form (described below) was fed to a laboratory-built potentiostat based on operational amplifiers. The choice of solid-state devices for its construction was made according to the following specifications:

(i)   high bandwidth (50–100 MHz),
(ii)   high slew rate (250–1000 V/μs),
(iii)   fast settling time (1% in 60 ns),
(iv)   low output impedance (20–100 Ω at 10 MHz),
(v)   low input bias and offset currents (± 1 mV and 50–100 pA, respectively).

Our circuit uses Burr-Brown 3342 operational amplifiers (the potential control) and 3551 (the voltage follower and the current-to-voltage converter); both can be replaced by more recent equivalents. Details of the potentiostat circuitry are given in Appendix A.

The potentiostat output and the linear voltage were connected to two channels of a digital storage oscilloscope model LS130 Scope Station (LeCroy) for simultaneous registration. The oscilloscope chosen for our application operates at 100 MHz, equivalent to 200 megasamples/s. Both the function generator and the oscilloscope were interfaced to a 486-type personal computer by means of an IEEE488 GPIB card model PcLab818 (AdvanTech).

The electrochemical cell was an all-glass cell designed for handling sample volumes from 0.5 to 5 ml. The working electrode was a gold or platinum microelectrode with a diameter of 5, 10, 60 or 500 μm, sealed in a glass tube. The electrode was polished by alumina suspension and diamond paste, followed by thorough washing and drying. The auxiliary electrode was a cylindrical platinum net that symmetrically surrounded the working electrode. The reference electrode was a silver/silver chloride electrode in 1 M lithium chloride separated from the sample solution by a salt bridge. The cell was equipped with an inlet and outlet for argon, which was used for oxygen removal and overpressure of an inert atmosphere during measurements. Samples for testing the instrument were prepared as 5 mM solutions of ferrocene in a 0.3 M supporting electrolyte (recrystallized and dried tetrabutylammonium hexafluorophosphate) in acetonitrile. Ferrocene (Sigma) was used as received. Oxygen was removed from the samples by passing a stream of argon (Linde).

III. SOFTWARE

The communication between the user and the instruments was programmed in TurboVision Pascal, Ver. 6 (Borland International). Windows-style programs (MSDos) sim-

plify the routine experimental work. Large numbers of experimental parameters are usually entered at the beginning of a series of experiments; only a few parameters have to be changed between each run. The Turbo Vision approach allows entry points of each parameter to be accessed at random, which eliminates the burden of having to enter parameters that are not changed. Data are analyzed principally by importing current-voltage curves such as ASCII files to Origin spread sheets (Microcal Software). The piecewise polynomial interpolation program (see below) was written in Fortran (Microsoft).

A. Interfacing instruments through the GPIB

The instruments used in our application make it possible to use a wide variety of operating modes and hence manually adjusting them requires a certain amount of skill in electronics. Both the function generator and the oscilloscope offer remote operation. The built-in GPIB allows four-letter commands and parameters to be transferred. This is equivalent to manually setting panel buttons and switches from a computer to both instruments. The choice of operating modes for the cyclic voltammetry can thus be optimized and automatically preset by a computer program. Command transfer between the computer and instruments is largely facilitated by a ROM-resident driver supplied by the manufacturer. The address switch on the interface card has to be set properly in order to activate the Pascal driver. This driver takes care of the GPIB communication protocol and timing on the machine-code level. A high-level language program (written by us) only defines appropriate command strings for instruments, and it calls the corresponding driver routines. A typical procedure and its call are given in Appendix B. The Pascal program for user-to-instrument communication provides the following dialog boxes that can be randomly and repeatedly evoked until the exact experimental conditions are set:

(i)   documentation of the experiment (sample composition, type of electrodes, etc.),
(ii)   parameters of the potential scan, scan rate and timing,
(iii)   manual sensitivity settings,
(iv)   data storage (the file name and disk directories),
(v)   style of data display,
(vi)   the ''run'' command preceded by information on the current setting of the critical parameters that can still be modified by evoking some of the dialog boxes (i)–(v).

This program structure proved to be useful for time efficient the voltammetric experiments. The operator gets last-moment warnings of the parameters that are being chosen, which prevents any accidental runs that would lead to deactivation of the electrode surface.

B. Source of the linear voltage scans

Finding the source of a triangular shape of the potential E for voltammetry may seem like a simple task since almost any commercial oscillator can supply such output. The function generator can be set to a certain frequency, amplitude

and dc offset, however, this is not a suitable repertoire of parameters for a cyclic voltammetry experiment. The optimal choice of potential scan range is sought by an operator according to the observed location of current peaks on the voltammetric curves, whereas different kinetic features of these peaks are required to set an appropriate scan rate $v = dE/dt$. Therefore a free range of starting, vertex and final potentials may be selected for voltammetric experiments whereas the slope of the voltage change v has to be independent of the limits of the potential scan. The next experimental runs may entail varying the scan rate v while keeping the same potential limits. The linear voltage scan for computerized voltammetry is usually generated in a program loop which increments the potential value and transmits it at a selected constant rate to a digital-to-analog converter. Such an approach cannot be applied for the higher scan rates intended here because the program execution time imposes an inherent limit. The triangular output of the function generator DG340 (or of any similar commercial instrument) cannot be used for such purposes for another reason: its shape is always symmetrical. Experiments requiring a large potential span toward negative potentials would have to polarize the working electrode by the same span to positive potentials (and vice versa), which might inactivate the electrode surface by unintended generation of products. The dc offset feature of the generator is only partially able to overcome the problem. Often the potential range needs to be either slightly extended or reduced, however, such an adjustment would also change the scan rate. Making a set of comparable records at the same scan rates requires fine frequency readjustment. As a consequence, the time base and the trigger delay of the storage oscilloscope should follow the change of frequency. All in all, this makes experimental operations cumbersome and time consuming. In order to obtain easier, more user-friendly performance of fast voltammetric experiments, we connected the function generator and the digital storage oscilloscope to a personal computer by means of the GPIB interface card. A program was written which accepts user parameters for a voltammetric curve: the initial potential E_i, the first vertex potential E_1, the second vertex potential E_2, the final potential E_f and the scan rate v. Moreover, the waiting time at any of these potentials can be simply implemented. These parameters are used for the synthesis of an arbitrary wave form which is subsequently loaded to the function generator via the GPIB bus. Several precautions have to be handled by the program:

(i)   the arbitrary wave form (12 bit) should not exceed the range ± 2047 mV;
(ii)   the sum of the dc offset and the wave form should not exceed ± 5 V;
(iii)   the amplitude of the arbitrary wave form can only be defined as a peak-to-peak value;
(iv)   the frequency of the arbitrary wave form can be set as $40/n$ MHz (where n is an integer); hence not all the values of the scan rates can be achieved;
(v)   the potential increment ΔE can be as small as 1 mV for all scan rates up to 40 kV/s, however, for the

higher scan rates the program has to set a correspondingly larger increment that is still acceptable ($\Delta E = 5$ mV yields $v = 200$ kV/s).

The synthesis of the voltammetric wave form should also take into account the requirements of a convenient triggering mode of the oscilloscope. In practice, the potential scan can begin either positively or negatively and, similarly, the initial potential could be of either polarity. This diversity in experimental conditions could make reliable single-trigger operation of the storage oscilloscope rather complicated. The use of repetitive wave forms can help to adjust the triggering level, however, this is not recommended. Repetitive wave forms should be avoided, otherwise the most important measurement on a freshly prepared electrode surface may be lost. The best solution to the triggering problem is to offset the wave form in such a way that it always begins at a zero voltage level. The oscilloscope will then perform reliably by setting the trigger input to the ac coupling. Hence the E_i value is subtracted from all parameters of the potential; the arbitrary wave form always begins at the zero voltage level and the generator output is offset by E_i volts. The conversion of the scan rate v, specified by the user, to the frequency f, at which the function generator should operate, is simply $f = 1000 \times v$. The arbitrary wave form feature of DG340 requires the frequency at which each individual point is transmitted to be specified. Once the necessary parameters are loaded onto the function generator and onto the oscilloscope, the program can trigger a ''single shot'' output of the arbitrary wave form from the function generator. The first voltammogram can then be registered on a freshly activated electrode surface. If required, repetitive scan modes are also possible.

C. Data acquisition

Data acquisition may also seem to be a very trivial problem. Experience has shown how routine experiments can be very tedious when there is only manual setting of the oscilloscope parameters. The first voltammetric curve is often difficult to register on a freshly polished and activated electrode surface. If the oscilloscope fails to trigger during the very first scan, the whole re-activation of the working electrode has to be repeated. Sample contamination is always a risk. Inappropriate timing of the storage oscilloscope often causes incomplete registration of the curve. We tested various trigger modes and levels appropriate for a large range of scan rates. On the basis of these preliminary tests, the program determines the optimum values of the time base (T_B), the pre-trigger delay (T_D), the trigger mode, the trigger coupling filters and the trigger level (T_L). The oscilloscope timing is derived from that frequency f which corresponds to a desired scan rate:

$$T_B = 10^4/f, \quad T_D = -T_B/10.$$

A safe absolute value of the trigger level is 0.1 V and either a positive or negative sign is set for each initial scan direction. A positive or negative trigger slope is likewise selected by an edge-triggered mode of operation. The trigger coupling

is set to ''ac bandwidth limited'' mode because other coupling modes have occasionally led to triggering problems.

IV. RESULTS

We now describe the results of testing the performance of our experimental setup and data-smoothing procedures. The measurements of fast cyclic voltammetry are usually tested on a fast reversible electrochemical redox system. The reason for this is that such a reversible system should theoretically yield well known parameters and peak shapes. A failure to observe theoretical curve shapes suggests limited instrumentation performance. The oxidation of ferrocene is one of the most frequently used redox couples for such a purpose. Here we present the results obtained in a 5 mM solution of ferrocene and 0.3 M of tetrabutylammonium hexafluorophosphate in acetonitrile. Our initial concern was with the the quality of the electronic circuitry and the time lag. The performance of our circuit was tested using measurements of the impedance spectrum of a 10 kΩ dummy cell. This test showed that the potentiostat introduces a phase shift of less than 5° at 100 kHz and at the highest gain. Hence, it performs better than expensive commercial instruments. Tests of the bandwidth based on the sine-wave signal cannot clearly reveal overshoots, which are often encountered when triangular or square-wave signals are applied. Furthermore, tests should be performed in such a way that operational amplifiers do not drive a dummy cell as the test load, but rather the actual loading impedance, imposed by an electrochemical cell. In our view a more appropriate test would be to compare the input triangular wave form applied to the electrochemical cell (filled with the ferrocene sample) with the corresponding real potential wave form, sensed by the voltage follower. Such conditions are more demanding but they also take into account the efficiency of the compensation of the ohmic drop. The results obtained at the highest scan rate of 200 kV/s are given in Fig. 1. The performance is satisfactory: there is a minimum delay of 130 ns at switching points of the triangular wave function; also there is no superimposed ringing or any kind of distortion of the linearity. The absence of potential instabilities is a prerequisite for achieving a reasonable current response.

Typical examples of experimental and simulated[10] cyclic voltammograms of ferrocene in acetonitrile are given in Figs. 2 and 3. The forward and backward scans yield oxidation and reduction current peaks, respectively. If the experimental setup performs correctly, the curves should comply with the reversible character, which is claimed by other authors. One experimentally observed difference between cathodic and anodic current peaks ΔE_p is related to the rate of the electron transfer reaction.[11] The value of ΔE_p can be distorted by incomplete compensation of the solution resistance, causing an error in the determination of the standard heterogeneous rate constant k^0. Hence, the comparison of values obtained by the present instrumentation and values reported by other authors can be considered as a quantitative measure of the quality of our setup. Experimental and theoretical peak shapes (Fig. 2) agree well at $v = 10$ kV/s, whereas at the upper scan rate limit a correction for the solution resistance
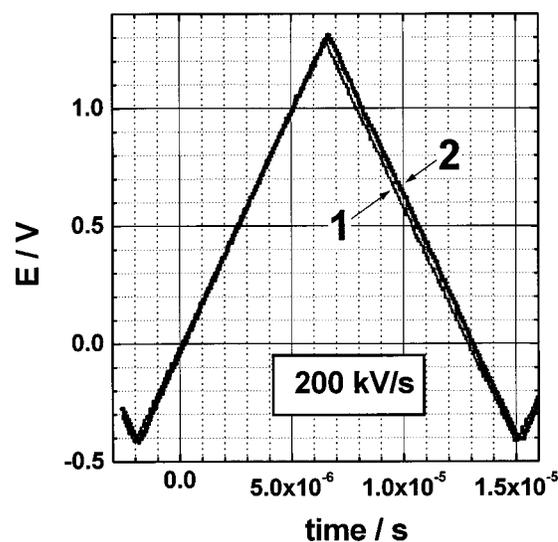
FIG. 1. The comparison of the input triangular voltage (curve 1) with the output voltage of the potentiostat follower (curve 2) under the conditions of an electrochemical experiment. The potentiostat was connected to the cell containing solutions of 5 mM ferrocene and 0.3 M tetrabutylammonium hexafluorophosphate in acetonitrile. The amplitude and the frequency correspond to the voltage scan rate 200 000 V/s.

must be taken into account (Fig. 3). The faradaic peaks at 200 kV/s are already distorted. Nevertheless they could be used for qualitative detection of short-lived intermediates at this rate. The dependence of ΔE_p on the scan rate v is shown in Fig. 4 together with a simulated curve. It yields an estimate of the standard heterogeneous rate constant $k^0 = 0.8$
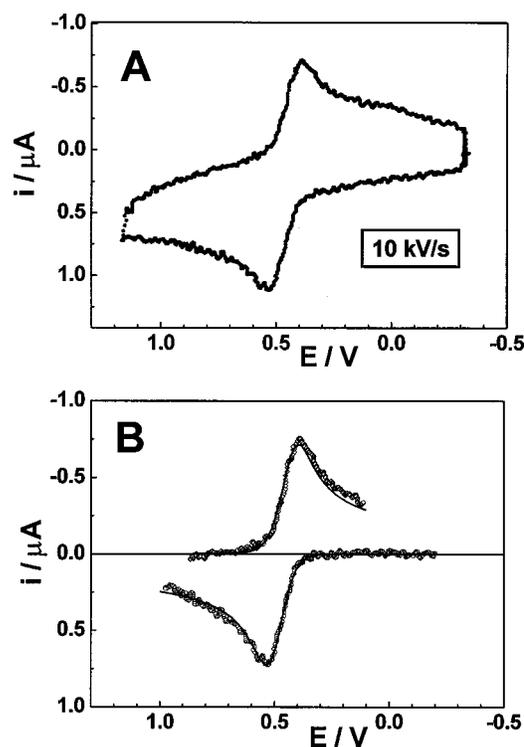
FIG. 2. Cyclic voltammetry of 5 mM ferrocene and 0.3 M tetrabutylammonium hexafluorophosphate in acetonitrile measured at a scan rate of 10 000 V/s on a Pt electrode of 10 μm diameter: (A) experimental voltammogram, (B) base line corrected faradaic peaks (points) and simulated theoretical curves (lines) for $k^0 = 0.8$ cm s^{-1} and $\alpha = 0.5$.
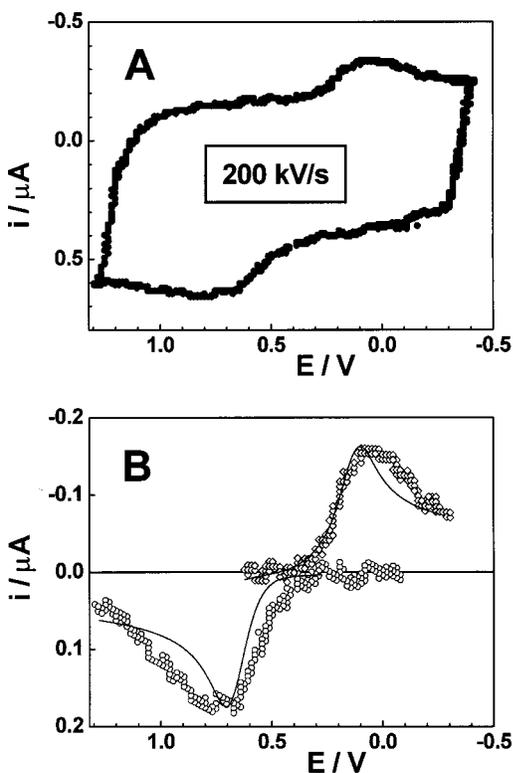
FIG. 3. Cyclic voltammetry of 5 mM ferrocene and 0.3 M tetrabutylammonium hexafluorophosphate in acetonitrile measured at a scan rate 200 000 V/s on a Pt electrode of 10 μm diameter: (A) experimental voltammogram, (B) base line corrected faradaic peaks (points) and simulated theoretical curves (lines) for $k^0 = 0.8$ cm s^1, $\alpha = 0.5$ and uncompensated resistance 78 Ω.

± 0.1 cm s^{-1}. The measurements of k^0 of the ferrocene couple have been made over the last two decades and the reported values from different laboratories[12–18] range from 0.02 to 3.1 cm s^{-1}. Adsorption of impurities and incomplete compensation of the solution resistance are considered to be major reasons for erroneously low values. Wightman and co-workers[19] found k^0 of ferrocene on a Au electrode was 3.1 cm s^{-1}, whereas the value on a Pt electrode was 0.95 cm s^{-1}. In this respect our value on a Pt microelectrode agrees reasonably well with the results of Wightman and co-workers.
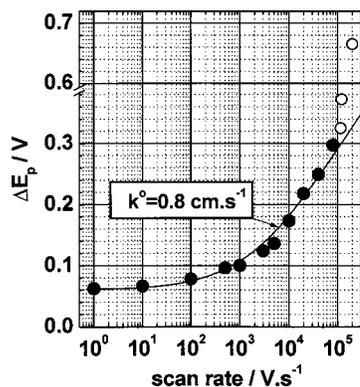
FIG. 4. The experimental dependence of the separation of anodic and cathodic peaks on the scan rate. The full curve is a simulated dependence for the value of $k^0 = 0.8$ cm s^{-1}. Open points represent data where the correction for uncompensated solution resistance should be applied.
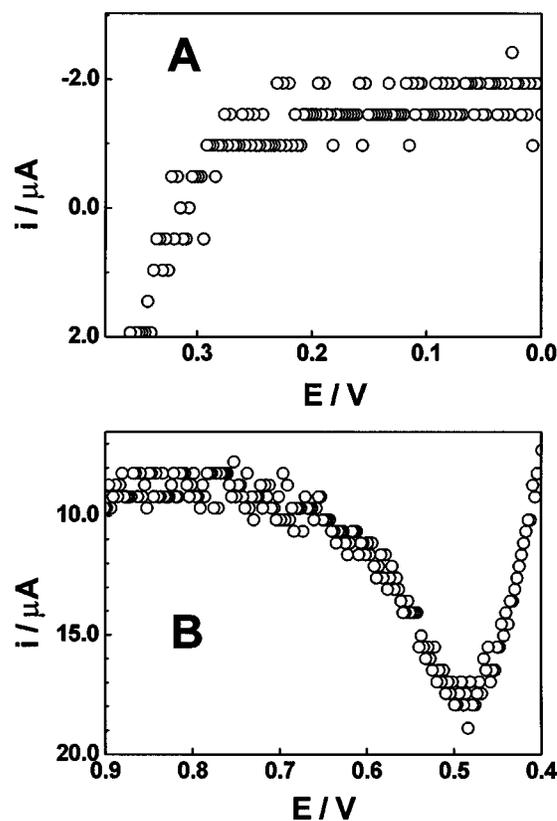
FIG. 5. Experimental uncertainty of the current measurements with an ultrafast digital storage oscilloscope operating with an 8-bit analog-to-digital converter. (A), (B) Data scatter at the foot of the voltammetric peak and near the current maximum, respectively.

Depending on the concentration and on the scan rate, the problem of low-level noisy signals is often encountered. The signal-to-noise ratio can be improved either by analog filters applied prior to registration, or by digital postfiltration of stored digital data. In principle, both methods should yield the same improvement but equally the same distortion of the resulting curve shapes. We considered it more appropriate to record raw nonsmoothed data and to apply an efficient postsmoothing procedure. This precaution is used in order to avoid irreparable distortion of unique measurements, sometimes made on rare samples. We found that the data scatter is caused mainly by the 8-bit resolution of the digital oscilloscope. Figure 5 shows two details of a current-voltage curve. The uncertainty of the 8-bit analog-to-digital (A/D) converter can be clearly seen. Since the sampling time base is precise, the observed data are horizontally spread along the potential axes. This creates a problem for data-smoothing procedures which are part of many spreadsheet programs (here we used ORIGIN). What is seen is a distribution of times for which a given analog level is detected by the A/D converter. Four different methods of smoothing were tested for the simplest routine performance:

(i)   adjacent averaging of three to nine points of the current versus potential curves;

(ii) exchange of axes both for current versus time and potential versus time records, followed by separate adjacent averaging of each record prior to plotting a voltammetric curve;
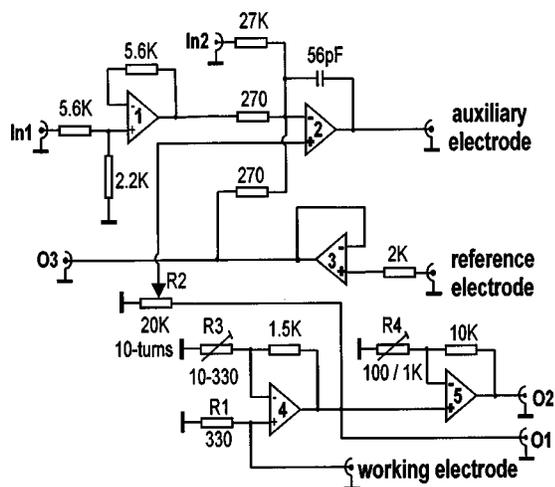
FIG. 6. Scheme of a potentiostat for fast voltammetric measurements (see the text).

(iii)　addition of random noise to experimental data followed by filtration;

(iv)　linear regression of individual segments of the voltage scan;

(v)　piecewise polynomial interpolation (PPI).

Method (i) gave very poor results and often introduced small but visible interference oscillations. Method (ii) is the simplest and yields acceptable results. Method (iii), recommended by Horlick,[20] turned out to be rather laborious and smoothing was achieved only at the expense of substantial data distortion. Method (iv) in combination with adjacent averaging of current data gave better smoothing than the aforementioned methods. However this method is cumbersome because the regression has to be performed step by step for every interval between potentials E_i, E_1, E_2 and E_f. The best performance was obtained by application of piecewise polynomial interpolation[21,22] to both the voltage versus time and current versus time records. The voltammograms were subsequently plotted on the basis of a smoothed data set. The PPI algorithm is similar to the Savitzky–Golay method. It performs local polynomial regression which determines a smoothed value for each data point. Unlike the Savitzky–Golay procedure, however, the polynomial degree is a variable for each data point. The degree of the interpolating polynomial is determined on the basis of adjacent data on both sides of a particular point.

The application of PPI procedures to all data points is repeated six times and each time the number of adjacent points for the determination of the optimum polynomial degree is changed according to the scheme 2-2-3-4-2-2 points.[2] We can conclude that smoothing method (ii) is good for routine work while method (v) is suitable for a final smoothing of important data.

The approach to fast cyclic voltammetry on microelectrodes (Fig. 6), described here, reduces the investment cost to approximately one third of the price of a fully commercial setup. Transparent source coding of a controlling program enables us to tailor the software for future nonstandard experiments. Applying the ferrocene redox couple yielded sufficiently similar results to those reported by other laboratories. The technique described here was applied to the identification of short-lived radicals in the field of organometallic redox processes[23] and also to decomposition reactions of pesticides,[24] as we have previously demonstrated in other papers.

ACKNOWLEDGMENTS

APPENDIX A

The design of our homemade potentiostat follows well-established principles for such circuits and is shown in Fig. 6. Here, we use Burr-Brown ultrafast operational amplifiers mounted on a small board which can be placed close to the electrochemical cell. Operational amplifier (OA) 1 serves as an impedance buffer. OA2 is a Burr-Brown 3342 fast settling line driver controlling the applied potential. OA3 is the voltage follower and its output O3 is used for recording the potential. OA4 is the current-to-voltage converter yielding a voltage proportional to the cell current to the measuring resistor R1 and amplified by the ratio of 1500/R3. The signal proportional to the cell current is recorded either directly (output O1) or after postamplification by factor of 10 or 100 at output O2. The best gain selection values for work with electrodes were in the range of 5–500 μm in diameter. Postamplification by 10 or by a 100 can be bypassed if the highest scan rates are used; this then eliminates a possible additional delay by an operational amplifier which is not needed for large signals. The attenuated input ''In2'' and the potential output ''O3'' were applied by impedance measurements. Under certain demanding conditions, such as high scan rates, the choice of components and their placement can either improve or can cause the circuit performance to deteriorate.

APPENDIX B

An example of a program segment written in Pascal that controls a wave form generator by transmitting commands via the GPIB interface shows that a complicated task of the data exchange protocol is substantially simplified by driver routines supplied by vendors of the interface card.

```
Program CyclicVoltammetry;
Uses Overlay, Objects, Drivers, Views, Menus, Dialogs, App, Crt, Graph, Dos;
 {$I  D:\TP\HPIB\TBPGPIB.INC}                        (*include calls to GPIB driver*)
 {$F+}
 Const AddressGenerator =23;                         (* function generator DS340 *)
       MyAddr          =21;                          (* PcLab IEEE card*)
       AddressLeCroy   =14;                          (* LeCroy storage oscilloscope *)
Var Potential: ARRAY[1..16000] OF integer;
     N        : integer;                             (* number of points in an arbitrary
 waveform *)
 •

 •

 •
Procedure Set_Waveform( var Potential: ARRAY[1..16000] OF integer;
                            var N: integer);
(* procedure loads the arbitrary waveform to the function generator*)
 var outstr : lstring;                               (* long string defined in the ROM driver *)
     i       : integer;
   length   : string;

 begin

   outstr:='FUNC5';                                  (* set generator to arbitrary waveform
                                                      according to manufacturer's specifications *)
   ieoutput (AddressGenerator, outstr);              (* call driver output to GPIB *)
   Str (N, length);
   outstr:='LDWA'+length;                            (* tell generator to accept data of a given
                                                      length; the
                                                      mnemonics follows manufacturer's command
                                                      list *)

   ieoutput (AddressGenerator, outstr);
   for i:=1 to N do
   begin
         Str(Potl[i], outstr);       (* converts a single potential point to an ASCII string prior to transmission *)
                ieoutput (AddressGenerator, outstr);       (* call driver output to GPIB *)
     end;
 end;
(* ------------main program-------------*)
 begin
 •                                                   (* values of Potential[i] have to be assigned *)
 •
Set_Waveform (Potential, N);           (* loads the arbitrary waveform to the function generator *)
 •

 •
end.
```

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