A Complete Instrument Design for Electrochemical Measurements with Ultramicroelectrodes

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Descreve-se um instrumento com interface para um microcomputador IBM-PC , consistindo de um programa em linguagem basic, uma interface de conversão e controle e um seguidor de corrente do tipo picoamperímetro. O instrumento possibilita a execução das técnicas voltamétricas mais usuais, em sistemas de dois eletrodos com eletrodo de trabalho do tipo ultramicroeletrodo. As técnicas voltamétricas podem ser aplicadas com velocidades de varredura de potencial de até 20 V/s, enquanto técnicas em que são utilizados transientes de potencial permitem a aquisição de dados em tempo mínimo de 250 ms. O programa de operação contém facilidades para o manuseio e tratamento de dados experimentais. Testes de funcionamento do instrumento, o acoplamento com sistemas eletroquímicos comerciais e alguns processos de montagem de ultramicroeletrodos são discutidos.

This work describes an IBM-PC interfaced instrument, that consists of a basic program, a converter interface and a current follower. The instrument provides facilities to perform most of the usual electrochemical and electroanalytical techniques on a two-electrode cell with an ultramicroelectrode. The voltammetric techniques can be applied using scan rates as high as 20 V/s, while transient techniques allow data acquisition at times as short as 250 ms per data point. The basic software allows several operational facilities in data treatment and handling. Performance tests of the different instrument functions, the coupling of it with commercial electrochemical instrumentation and some description of ultramicroelectrodes fabrication are discussed.

Key words: *ultramicroelectrodes; electrochemical instrumentation; voltammetric techniques.*

Introduction

The nowadays widespread use of ultramicroelectrodes probes, in various types of electrochemical and electroanalytical applications, and the growing number of potential uses for it can be easily verified. Ultramicroelectrodes have several advantageous characteristics that are reported in many papers in the literature[1-4].

The most frequently used ultramicroelectrodes are based on platinum, gold and carbon, mainly in disk-form, insulated in glass or epoxy resins. In this context, also for the instrumentation requirements many advantages can be visualized. The use of little two-electrode cells with small solution content, allows substantial savings in high price materials and reagents.

The present paper describes an instrumentation system that includes a Basic and Assembler edited computational program. The program acts over an Analog to Digital and Digital to Analog interface converter, adapted directly at the main board of the microcomputer. The interface supplies the digitally generated potential functions that are applied to the working electrode, and measures the current responses signals amplified by a current follower.

The electrochemical techniques included in the software are; cyclic voltammetry, linear stripping voltammetry, differential pulse stripping voltammetry, square wave voltammetry, double step chronoamperommetry, an automatic data acquisition system for Tafel plots, and control possibilities for switching current scales, cell current and other experimental functions. The instrumentation system can also be coupled to commercially available potentiostats and polarographic analyzers thus avoiding the use of the current follower and recorder devices.

The fabrication of disk shaped ultramicroelectrodes using platinum wire (25 microns diameter) and carbon fiber (7 microns), sealed in neutral and Pyrex glasses will also be described. Insulation of both electrode materials in epoxy resin is another possibility.

The characteristic responses of platinum ultramicroelectrodes for $Fe(CN)_6^{3-}$ reduction and for the hydrogen evolution reaction in acidified aqueous solutions will be presented as illustration.

Software Description: the program AVOLM was written in BASIC using high resolution graphics features and can be executed in Quick-Basic (vers. 4.5, Microsoft) interpreter, using MS DOS operating system. The software occupies about 110 kbytes of memory. Except by a few reserved data bus address memory the interface does not interfere with the general use and other applications of the computer.

Two Assembler edited sub-routines executed in Macro Assembler interpreter, allows A/D and D/A conversions steps to be linked to the main program module. These routines are linked using the Microsoft Linker software. The software allows data files characteristically containing one thousand data pairs to be saved under the ASCII code or as a binary file. Data files containing at its end a complete list of the experimental parameters can be reloaded for subsequent analysis. Once started the program automatically read a file containing default parameters that can also be changed and saved. High resolution graphics for the different experiments can be obtained by the print screen function.

Digital data can be directly handled on the screen by pointing with a graphic cursor and selected areas can be easily integrated to provide charges in current-time experiments. The program also provides a smoothing data facility in accordance with Savitzky and Golay[5]. Moreover, the ASCII data files can be easily recovered and treated by other software packages.

Interface specifications: the Tango-PCB Layout System (Protel Systems Pty. Ltd./ ACCEL Technologies, Inc.), was used to design the converter interface, which was screened in a double layer board. The A/D and D/A twelve-bits converter uses the chips AD-574A-KD and AD-7543 KN. Twenty-four TTL level control channels are provided by the use of a dedicated ordinary 8255 chip.

The D/A potential source can apply a range of potentials of $^{+}$/- 10 volts, driven by an OPA27GP at low current levels with high precision and stability. Presently, both conversion steps are adjusted to operate in the $^{+}$/- 2,048 mV range for the necessary accuracy to be provided by the twelve-bits converters. The $^{+}$/- 15 volts required by the signal amplification stages are given by an on board supply feed by the computer. Despite the high nominal speed (25 ms) of the A/D converter, at the moment the conversion limit is fixed by the basic/assembler software and the computer clock at a rate of 250 ms by conversion. At this limiting rate it is possible to drive cyclic voltammograms at 20 V/s, with sufficient data points (and potential steps), to give accurate interpretation of the experiments up to one volt in the potential range.

Current follower specifications: a prototype current follower amplifier was constructed to operate connected to the interface described above, having an output of one volt in each full scale. The scales, in number of six, range from 100 pA to 1 mA. A balancing panel potentiometer allows zero adjust for the output at each current range. Other facilities such as automatic scale switching, manual cell on/off switch, analog output display, and recorder output are also provided.

A precision amplification circuitry based on the OPA128 feed by a stable optically isolated power supply provides a clean amplified DC output for all scales with the exception of the most sensitive one, where an additional RC filter properly chosen is coupled. The low level current ranges are calibrated by the use of a precision current source based on the REF200AP from Burr-Brown[6].

Microvoltammetric electrodes: the 25 mm diameter platinum wire (Johnson & Matthey, Inc.), as well as platinum wires of other diameter sizes, are easily sealed on neutral and Pyrex glass capillary tips on a reducing flame to produced well sealed disk-shaped microelectrodes. The electrode tips were polished on abrasive wet paper of decreasing particle granule, and then on wetted alumina powder down to 0.05 mm. After cleaning by washing, the electrodes are ready for use. The electrode contact was made using a conducting silver glue (Degussa, s.a.), and larger diameter copper wires.

Carbon fiber disk-shaped electrodes were mounted in the same way described before, but the sealing procedure was carried out under vacuum. These microelectrodes were constructed with 7-8 mm diameter carbon fiber (CTA - S.P.)

Microvoltametric electrodes of the two materials described above have also been easily made by sealing on epoxy resin (Reforplas s.a.), with suffices for most aqueous applications. It is also possible to grow mercury drops on the platinum microdisks thus allowing its use in several electroanalytical applications.

Experimental

All reagents used to perform the apllication examples showed here were Merck Suprapur. The reference electrodes used were small size $Ag/AgCl_{(s)}$ or $Pt(H_2)$ electrodes. A specially constructed 3 ml Teflon cell was employed in the voltammetric experiments All experiments were conducted with the cell protected by a Faraday cage.

Functioning characteristics and applications: the response time of the conversion steps can be evaluated by the dummy cell responses registered in Figure 1 for a double step potential jump. In this figure, the effect of one capacitive noise filter, used in the lowest current range, is evident.

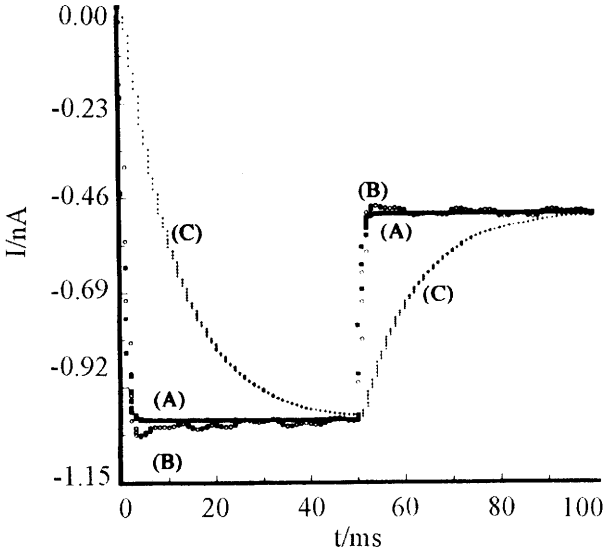

Figure 1. *Response tests for potential steps (dummy cell 500 MOhm (5%)). (A) interface, (B) current follower.without filter and (C) current follower with RC filter.*

Figure 2 shows a Tafel plot for the hydrogen evolution reaction, obtained with the aid of the instrumentation described above, on a Pt microdisk (F=25mm) sealed in Pyrex glass, in 0,5M H_2SO_4 solution at 25^{o} C. This experiment shows some of

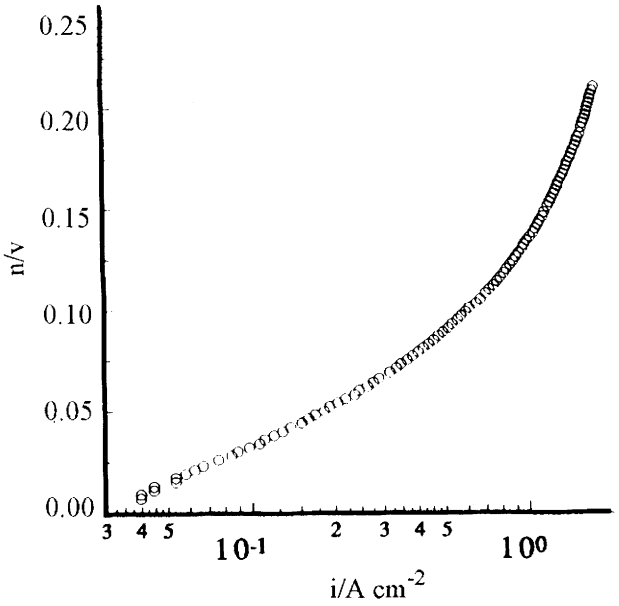

Figure 2. *Tafel plot for the hydrogen evolution reaction on a platinum disk (F=25mm) ultramicroelectrode in 0.5 M H_2SO_4 solution at 25° C.*

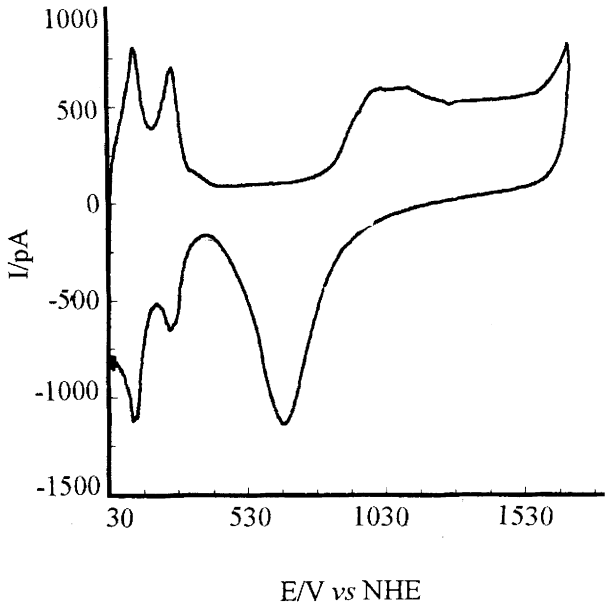

Figure 4. *Cyclic voltammetric response of a 25 mm diameter platinum disk in 0.5 M H_2SO_4. Scan rate 10 V/s.*

the advantages of using ultramicroelectrodes for kinetic studies such as the possibility of applying currents of the order of 2 A without any evidence of bubbles nucleation or ohmic potential drop.

The stationary response obtained for the carbon microdisk (Figure 3), for the voltammetric reduction of 5 mM potassium ferricyanide in acidified solution, confirms the proper isolation of the carbon fiber ultramicroelectrodes mounted in Pyrex glass as described before.

Figure 4 presents the platinum microdisk electrode surface behavior in a H_2SO_4 (0.5 M) solution, at a scan rate of 10 V/s.

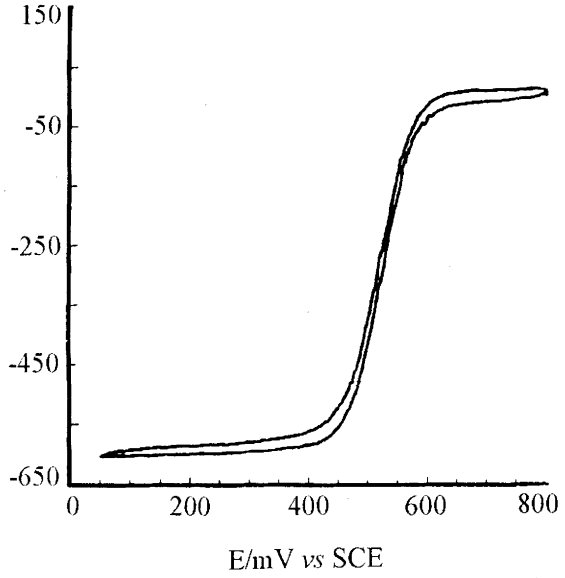

Figure 3. *Cyclic voltammetry for potassium ferricyanide (5mM) reduction on a 7 mm diameter carbon electrode. Scan rate 10 mV/s, pH 3.*

As it can be observed, the described instrumentation design is also useful to study electrokinetic phenomena.

Conclusions

As shown by the performance tests (Figures 1-4), the instrumentation design described here works very well in the time domain applied. The practicallity of the software under use is very great if it is compared with conventional instrumental equipments. Therefore it have been very well accepted by many users in our labs. Eventual modifications and/or faults can be promptly considered in new versions of the basic program.

It can be concluded that the possibility of executing digitally programmed electrochemical experiments is the most important feature of this cheap instrument design. The facilities for data handling, and the intelligent interface available to the user, are also important characteristics when using this type of instrumentation.

More detailed characteristics of the system can be obtained from the authors on request.

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