Low cost potentiostat: Criteria and considerations for its design and construction

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Abstract:
This article shows the construction of an inexpensive potentiostat, considerations and criteria to be taken for manufacturing it. General purpose and low cost electronic devices were used in this proposal. Excellent results for square wave voltammetry (cyclic voltammetry) were gotten against a commercial potentiostat, this technique is basic and very widely used in the field of electrochemistry.

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Keywords

IEEE Keywords
Electrodes, Electric potential, Voltage measurement, Current measurement, Passive filters, Digital filters, Active filters

INSPEC: Controlled Indexing
voltammetry (chemical analysis), potentiometers

INSPEC: Non-Controlled Indexing
electrochemistry, low cost potentiostat, general purpose, low cost electronic devices, square wave voltammetry, cyclic voltammetry

Low cost Potentiostat: Criteria and considerations for its design and construction

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Abstract— **This article shows the construction of an inexpensive potentiostat, considerations and criteria to be taken for manufacturing it. General purpose and low cost electronic devices were used in this proposal. Excellent results for square wave voltammetry (cyclic voltammetry) were gotten against a commercial potentiostat, this technique is basic and very widely used in the field of electrochemistry.**

Keywords—potentiostat, volammetry; filters; operational amplifiers; STM32F407.

I. Introduction

In the branch of electrochemistry, the potentiostats allow the study of redox processes at molecular level. These devices are irreplaceable in different fields of research, such as: qualitative and quantitative analytical electrochemistry of organic molecules (e.g. drugs) [1] and inorganic (e.g. heavy metals) [2], even at levels of trace, in environmental monitoring [3], in the construction and characterization of sensors and biosensors [4], among others. Potentiostats can work in processes with controlled current, which generally uses two electrodes (work and counter electrodes) in cell, or processes with controlled potential, where it is necessary to work with three electrodes (working, counter and reference electrode) in cell [5].

In electroanalytical processes (processes with three electrodes) the potentiostat generates a difference of potential between the working electrode and the reference electrode, to achieve this, the voltage between the working electrode and the counter electrode must be controlled. So, it is a tool that allows to set or vary the potential (potential sweeps) of a working electrode respect to the reference electrode at any time, regardless of the current required to achieve that objective [5].

Due to the high demand in the scientific community and the high price of this device, nowadays is much cheaper to build it, using existing information [6, 7]. Rather than, it is important to mention that homemade potentiostats have error and can't achieve the features of a commercial potentiostat, the cheap potentiostats built today, and whose can approach the commercial features are the CheapStat [6], DStat [7] and the built in this work.

The quality, accuracy and precision of the potential waves, as well as the potential and current measured in electrochemical experiments, depend mainly on the implemented 'Hardware'. Which can be affected by materials used (integrated circuits, resistors, capacitors, etc.), the design of the PCB (Printed Circuit Board), the manufacturing of PCB and finally how the elements were mounted [8].

Based on these criteria, the present research proposes an alternative design of the low cost hardware for potentiostat, which is able to run cyclic voltammetry measurements. The response of the equipment must be checked by using a Platinum working electrode and a solution of 0.1 M potassium ferricyanide/ferrocyanides (the two redox pairs). In addition, the obtained signals will be compared with signals from a commercial potentiostat CHI-DY2100B.

II. General Aspects

Before choosing the electronic elements, it is important to set a general idea of the necessary stages, which must be implemented to achieve reliable electrical signals, as shown in Fig. 1 [5]. With the selected items, it is possible to give way for methodology and basic considerations to built a low cost potentiostat.

III. Considerations and Criteria

Hardware of a potentiostat is basically divided into two stages, generation and measurement of voltage, and current measurement; as shown in Fig. 1.

In the first stage, the circuit shown in Fig. 2, is the main circuit of a potentiostat, because it allows to fulfil the necessary conditions for its operation, which are:

- Control the potential between the working electrode and the reference electrode.
- Avoid the flow of current between the counter electrode and reference electrode.

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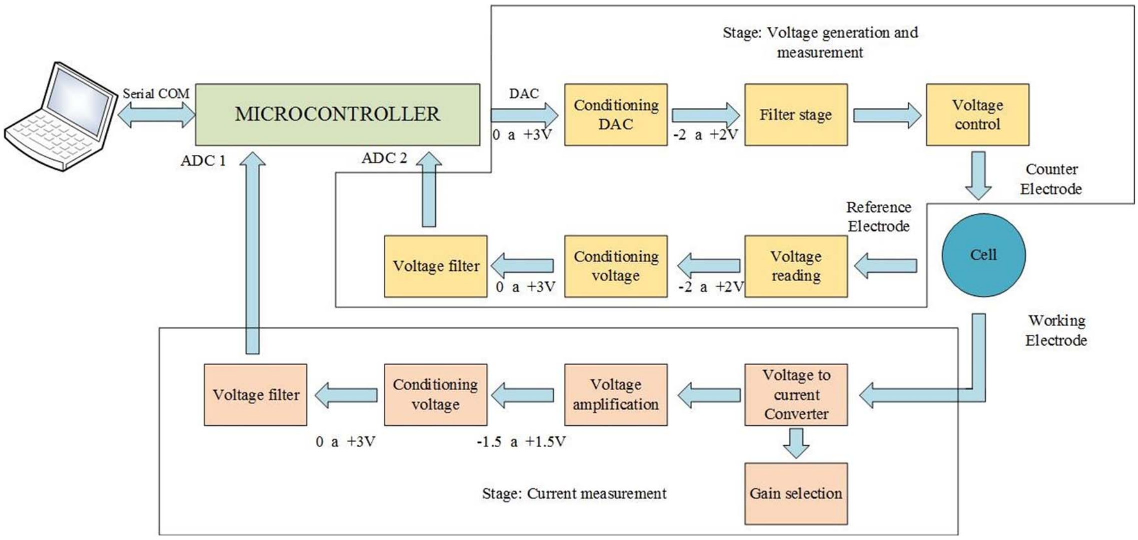

Fig. 1 Block diagram of the proposed hardware.

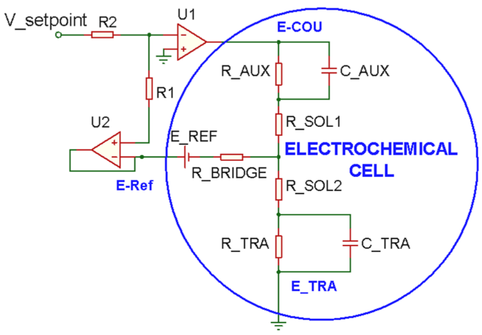

Fig. 2 Stage: voltage generation and measurement.

Analyzing the circuit of Fig. 2, the operational amplifier (op-amp) U1 is feedback by: R1, U2, E_REF, R_Bridge, R_SOL1 and (R_AUX || C_AUX). Subsequently, taking into account that the potential difference between the positive input and negative input of an operational amplifier is ideally zero, the negative input of the op-amp U1 is grounded; under the same premise the negative input of U2 has the same electrode potential reference.

The circulating currents by R1 and R2 are given by the Eq. (1), and the Eq. (2), respectively.

$$I_{R1} = \frac{V_{ERef}}{R_1} \quad (1)$$

$$I_{R2} = \frac{V\_setpoint}{R_2} \quad (2)$$

Therefore, the current flowing through R1 is equal to the current that flows by R2 [15], and if R1 is equal to R2 then slogan voltage (V_setpoint) will be equal to the potential on reference electrode. So, U1 must supply the necessary current according to set voltage, to keep the potential between the working electrode and the reference electrode [5].

Once control of potential between electrodes work and reference has been achieved, the flow of current between the counter electrode and reference electrode must be avoided; this is accomplished by op-amp U2. This is configured as a voltage follower, reducing the flow of current to the maximum allowed by the op-amp (Input Vias Current), ideally zero [15].

Met these two conditions, it is possible to perform the measurement of the potential at the working electrode, but measured voltage is given by the Eq. (3).

$$V_{Measured} = E_{ET} + E_{ER} + R_U * I_{Cell} \quad (3)$$

Where:

$V_{Measured}$ = Voltage measured by the implemented system.

E_{ET} = The working electrode potential.

E_{ER} = Reference electrode potential.

R_U = Resistance of the dissolution.

I_{Cell} = Current flowing through the three-electrode cell.

Based on the Eq. (3), compensation of the measured voltage must be taken to adjust this to the real value of the potential in the working electrode.

The measured voltage compensation consists of subtracting this: the value of the potential of the reference electrode and the value of the fall of potential due to the solution.

Implemented potentiostat just compensates the reference electrode potential, and the fall of potential due to the solution was not compensated because its incidence in the experiments to be run out is not significant [14].

In the second stage, the current that flows between the counter electrode and working electrode during electrochemical experiment is measured.

Fig. 3, shows the circuit implemented to convert the current to voltage. This is necessary because converter (ADC) is used for measuring analog to digital current, but in fact measure voltage [9]. To determine the value of the resistance the Eq. (4) is used, but the C value is subjected to the conditions discussed in [13] and thus allows stabilize the current to voltage converter circuit.

$$V_{out} = -R1 * I\_in \tag{4}$$

To obtain the best resolution for conversion, current measurement, it is necessary to measure this in different ranges: 100 nA - 1 uA, 1 uA - 10 uA, 10 uA - 100 uA, 100 uA - 1 mA. To achieve that, it is necessary to use the digital switch (DG612), which allows change the current converter gain according to the measuring range.

In practice, a potentiostat has different problems [16], but one of the most important is its susceptibility to electrical interference (noise), which may be inherent to the electronic system, electrochemical cell, or environmental conditions. The way to reduce the effect of interferences in the measured signals is through the implementation of filters.

According to the experiments to be run out, it has determined working frequencies, these range are from 0.25 Hz (minimum rate) to the 10 Hz (maximum rate). With working frequencies, the type of filter is determined (Low Pass) and its cut-off frequency is 10 Hz.

The filter designed is: fifth-order Bessel with a quality factor of 0.58. Its response is shown in Fig. 4.

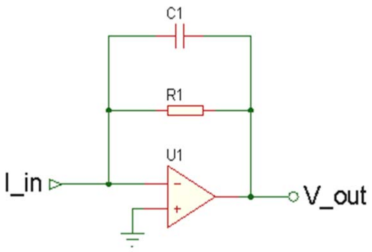

Fig. 3 Current to voltage converter.

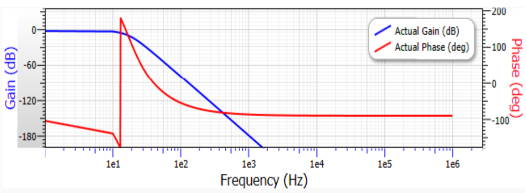

Fig. 4 Filter responce

The filter was introduced in previously described stages, fig. 5. displays the result of the filter.

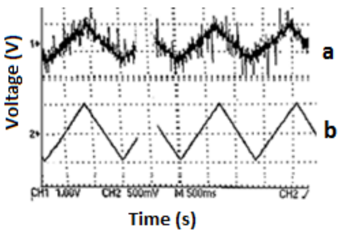

Fig. 5 a) signal prior to filtering, b) signal back to filtering

Because of the susceptibility that presents current stage, explained in [13], we implemented a passive filter (Low Pass). It is in series with an active filter (Bessel), in order to attenuate, even more, the noise in the current signal. Cut-off frequency for passive filter is 10 Hz and it was designed with criteria explained in [17].

IV. Results and Discussions

The first experiment was executed with a solution of potassium ferricyanide 0.1 M, this solution allows to get voltamperogramas, where you can see peaks of oxidation and reduction. In Fig. 6, is the result of the first experiment.

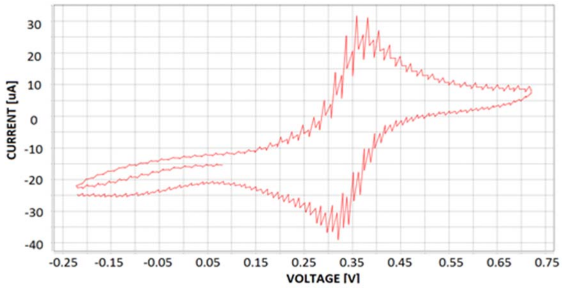

Fig. 6 Voltamperogram of the 0.1 M potassium ferricyanide using a working electrode of Platinum, a counter electrode of graphite, and electrode reference of Ag/AgCl, for the first experiment performed.

The first experiment presents a large amount of noise in the voltamperogram, Fig. 6, so the analog filters could not reduce the entire external or inherent interferences. After making several analyses the factors which produce the noise were found, these factors are inherent to the electronic circuit, mainly to the operational amplifiers.

According to the problems presented by the op-amps, the introduction of new analog filters will not reduce the noise, a good choice would be to change the operational amplifiers, but the system was already implement so it is not an option.

Therefore, a digital filter is the best option, a Kalman filter [11, 12]. The Kalman filter is a predictive/corrective filter and its constants were determined by the processing of data indicated in [12]. The Eq. (5), shows the design values.

$$\mathrm{xn} = \mathrm{xan} + 0.032 * (\mathrm{yn} - \mathrm{xan}) \tag{5}$$

Where:

Xn = predicted value.

Xan = previous predicted value.

yn = real current value.

Fig. 7, shows the result of Kalman filter in the signal of the Fig. 6.

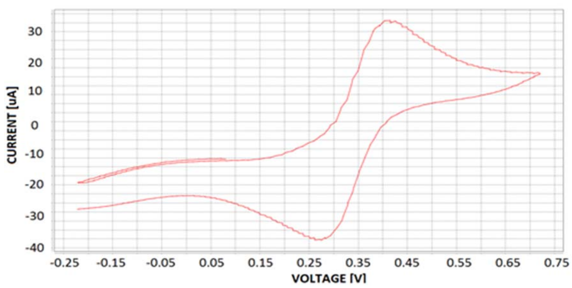

Fig. 6 Voltamperogram of the first experiment with the implementation of the Kalman filter.

Finally, a comparison between the signals of the implemented potentiostat and the commercial potentiostat was made. The results are shown in Fig. 10.

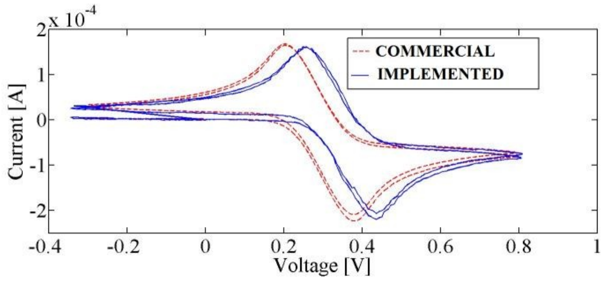

Fig. 10. Voltamperogram of the 0.1 M potassium ferricyanide using a working electrode of Platinum, a counter electrode of graphite, and electrode reference of Ag/AgCl. Implemented potentiostat vs commercial Potentiostat.

In Fig.10, there is a shift in the peaks of oxidation and reduction, this shift is due to a " parasitic resistance " of the built system, this resistance exits because there is an error in the design of the PCB which was not determined before and could not be fixed.

Other reasons why errors between the implemented potentiostat and commercial potentiostat signals are presented below:

- Operational amplifiers, resistors and capacitors are general-purpose, and may generate errors in the measurements.
- A Kalman filter was implemented, this filter is characterized as a corrective predictive filter with statistical sources. So this filter shifts the actual values of the Anodic and cathodic potentials.

It is important to say that implemented potentiostat is strictly for academic purposes, so the analysis and studies through it are demonstrative, allowing accept an error less than 30 %.

V. Conclusions

It was possible to build a potentiostat which is able to reproduce the response of oxidation and reduction through cyclic voltammetry, being this satisfactory in comparison with a commercial potentiostat.

The error, which can be appreciated in Fig. 10, corresponds to an error of 30% and is due to a parasitic resistance, which has not been fixed in this first prototype.

It has been implemented digital, active and passive filters, checking its great usefulness in engineering.

Using DACs and ADCs incorporated in a microcontroller can mean an advantage when implementing the PCB, but it is counterproductive in systems where required greater stability and robustness. Therefore, it is best to incorporate external DAC'S and ADC's to the microcontroller.

The construction of a low cost potentiostat, which achieved very good results in comparison with a commercial potentiostat, represents an important milestone, because it enables laboratories of low budget to perform general and basic electrochemical experiments.

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References

[1] King, D., Friend, J., & Kariuki, J. (2010). Measuring vitamin C content of commercial orange juice using a pencil lead electrode. Journal of Chemical Education, 87(5), 507-509..

[2] Forsberg, G., O'Laughlin, J. W., Megargle, R. G., & Koirtyihann, S. R. (1975). Determination of arsenic by anodic stripping voltammetry and differential pulse anodic stripping voltammetry. Analytical Chemistry, 47(9), 1586-1592.

[3] Lee, S. W., & Meranger, J. C. (1981). Determination of total arsenic species by anodic stripping voltammetry. Analytical Chemistry, 53(1).

[4] Fan, C., Plaxco, K. W., & Heeger, A. J. (2003). Electrochemical interrogation of conformational changes as a reagentless method for the sequence-specific detection of DNA. Proceedings of the National Academy of Sciences, 100(16), 9134-9137..

[5] Bard, A. J., Faulkner, L. R., Leddy, J., & Zoski, C. G. (1980). Electrochemical methods: fundamentals and applications (Vol. 2). New York: Wiley.

[6] Rowe, A. A., Bonham, A. J., White, R. J., Zimmer, M. P., Yadgar, R. J., Hobza, T. M., ... & Plaxco, K. W. (2011). CheapStat: An open-source,"do-it-yourself" potentiostat for analytical and educational applications. PloS one, 6(9), e23783.

[7] Dryden, M. D., & Wheeler, A. R. (2015). DStat: a versatile, open-source potentiostat for electroanalysis and integration. PloS one, 10(10), e0140349.

[8] M. I. Montrose, EMC and the printed circuit board: design, theory, and layout made simple, 2004

[9] Low Level Measurements Handbook: Precision DC Current, Voltage, and Resistance Measurements. Keithley Instruments, 2004.

[10] Johnson, D. E., & Hilburn, J. L. (1975). Rapid, practical designs of active filters. John Wiley & Sons.

[11] Cela, A., Yebes, J. J., Arroyo, R., Bergasa, L. M., Barea, R., & López, E. (2013). Complete low-cost implementation of a teleoperated control system for a humanoid robot. Sensors, 13(2), 1385-1401.

[12] Welch, G., & Bishop, G. (2006). An introduction to the kalman filter. Department of Computer Science, University of North Carolina.

[13] Kanazawa, K. K., & Galwey, R. K. (1977). Current follower stabilization in potentiostats. Analytical Chemistry, 49(4), 677-678.

[14] G. Instruments, "A basic understanding of iR compensation," in gamry. [Online]. Available: http://www.gamry.com/applicationnotes/instrumentation/understanding-ir-compensation/. Accessed: May 12, 2016.

[15] Robert, C., & Frederick, F. D. (1999). Amplificadores operacionales y circuitos integrados lineales. Editorial Prentice Hall Quinta Edición, México.

[16] Alcañiz Fillol, M. (2011). Diseño de un sistema de lengua electrónica basado en técnicas electroquímicas voltamétricas y su aplicación en el ámbito agroalimentario.

[17] R. Burt and R. M. Stitt, "Fast Settling Low-Pass Filter," in Texas Instruments. [Online]. Available: http://www.ti.com/lit/an/sboa011/sboa011.pdf. Accessed: May 16, 2016.

[18] Arévalo Ramírez, T., & Castillo Torres, C. (2016). Implementación de un potenciostato y de un nuevo software para el control y visualización de señales eléctricas generadas en experimentos electroquímicos