CONSIDERATIONS AND MEASUREMENTS REGARDING A DIDACTIC PORTABLE POTENTIOSTAT

L.M. RAB[1] **A. MUNTEANU**[1]

Abstract: *This paper presents the function, design and construction principles of a portable, inexpensive potentiostat. The presented device is designed for didactic study and researches. The considerations were based on study of potentiostatic control, including basic potentiostatic circuits and electrochemical applications. Commercially potentiostats are large in size and expensive. For these reasons, it was desirable to design and build a miniaturized, inexpensive field-portable potentiostat to interface with various types of electrochemical probes. The aim of this work was to offer this instrument as a laboratory experiment or special project for students.*

Key words: *potentiostatic control, portable potentiostat, electrodes.*

1. Introduction. History of Potentiostatic Principle

We will made an introduction to the principle of potentiostatic control, including basic potentiostatic circuits, electrochemical applications, and some notes on electrode and cell design [1]. Potentiostats are amplifiers used to control a voltage between two electrodes, a working electrode and a reference electrode, to a constant value (Figure 1).

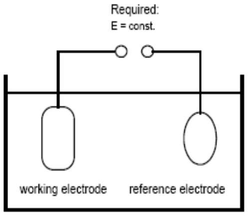

Fig. 1. *A simple electrochemical cell*

Let us have a look back into the year 1950. In this period, metallurgists and physic-chemists tried to bring some light into a fascinating electrochemical phenomenon. If you dip an iron wire into diluted sulphuric acid, it will instantly start to dissolve - it corrodes. If you now insert another electrode, which shall not corrode, e.g. platinum, and connect the iron electrode to the negative pole of a current source, and the platinum wire to the positive pole, the iron dissolution will slow down or even stop, depending on the voltage applied. If you connect the iron electrode to the positive pole, and raise the voltage from very low values to higher ones, the dissolution grows exponentially with rising voltage [2]. Above a certain current limit, depending on the electrode area and the electrolyte composition and the temperature, you find out that the current suddenly drops to very low values, and the iron electrode stops to dissolve. A better understanding was possible after invention of the potentiostat. The nature of the phenomenon imposes an electrochemical

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[1] Dept. of Electrical Engineering, *Transilvania* University of Braşov.

method to investigate. The idea was to record the characteristically current - voltage curve of the iron dissolution in the electrolyte. However, there was one difficulty: according to the applied method, the results varied strongly. If you control the current, using an adapted current source, and measure the voltage between the iron electrode and a reference electrode, you find that depending on the direction chosen to record the curve, you will obtain different results (Figure 2).

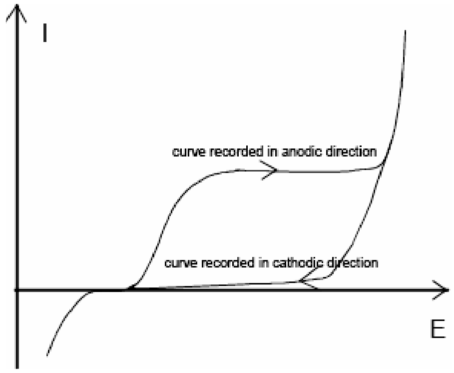

Fig. 2. *"Galvanostatically" recorded current - potential curve*

People tried to go the other way: to control the potential between the reference electrode and the iron electrode, while the current was measured. They used a low - ohmic voltage source to control the potential to a constant value. This method was applicable within certain potential regions. However, between the region of active dissolution and the passive region, oscillations occurred in an interval of some hundred millivolts [6].

The reason for these oscillations could be explained: The current in the active region before onset of passivity is roughly 5 orders of magnitude higher than in the passive region. A low - ohmic voltage source, which may have a source resistivity of 1 Ohm only, produces a potential shift of 100 mV back to the active state when the current is falling from 100 mA to 1 μA. A stable state cannot be achieved. So, it was not possible with manually controlled voltage sources to find the true current - potential curve which could help to clarify the mechanisms of passivation. D.C. amplifiers promised to bring a solution. Disregarding the difficulties of bulb - driven amplifiers which caused stability problems, these amplifiers showed systematic errors. The voltage difference between a stable reference - element is formed between the grounded working electrode and a reference electrode [4]. The first potentiostat built by Hans Wenking already showed the features which you find today in a common solid - state operation amplifier. This basic potentiostatic principle is used in many instruments until today [5].

2. Basic Theory of Potentiostatic Control

Electronic potentiostats are used for controlling the potential in an electrochemical cell.

The current in the cell from a counter electrode to a working electrode is controlled by means of the potentiostat so that the actual potential of the current - carrying working electrode relative to a current - free reference electrode follows a predetermined control voltage and is held constant at its instantaneous value irrespective of electrochemical processes. The ideal potential controller has an infinite gain and operates so that the difference between actual and control voltage disappears without any noise or disturbance being introduced. Potentiostats are amplifiers used to control a voltage between two electrodes, a working electrode and a reference electrode, to a constant value. To achieve this, some conditions have to be matched: reference electrodes are electrodes, which maintain a constant voltage referred to the potential of the hydrogen electrode. A silver wire, covered with a silver chloride layer, dipping in a chloride solution, is a simple reference electrode. How can we achieve to maintain a constant potential difference between the reference electrode and the working electrode? We are forced to introduce a third electrode, which we call counter electrode. A current is forced between working electrode and counter electrode, high enough and in proper polarity to keep the working electrode potential at a constant value with respect to the reference electrode (Figure 3).

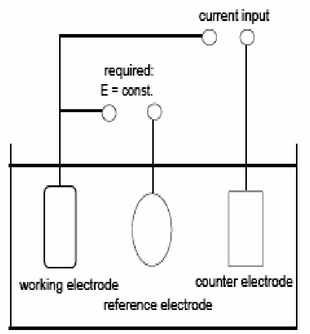

Fig. 3. *Principle of a potential - controllable electrochemical cell*

Potentiostats in their electronic action are identical with difference operational amplifiers whose power output provides voltage and current for the cell in the feedback loop. Unlike the usual application of operational amplifiers in which the feedback loop is determined by separate electrical components, potential control by potentiostats includes an electrochemical cell in the control loop whose impedance varies greatly with potential and time. Both the conductivity and the double layer capacitance of the boundary layer where the potential is being controlled, vary over many decades as the potential changes. Information on the electrical replacement circuit of the control loop is often available only after experimental results with controlled potential have been obtained. It is essential therefore, that the potentiostat provides sufficiently accurate and stable control of the cell potential over an extremely wide range of cell currents for extensive variations in the usual complex feedback circuit and in addition operates within a sufficiently short interval of time.

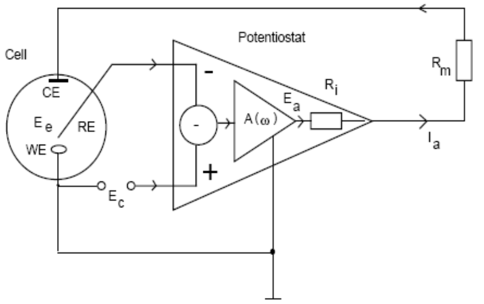

Fig. 4. *The schematic diagram of the potential control*

The potentiostat implements this control by injecting current into the cell through an auxiliary, or counter, electrode CE (Figure 4).

The input difference stage forms the difference $\Delta E = E_c - E_e$ between the control potential fed in at the non - inverting input (+) of the potentiostat, and the actual potential E_e between reference electrode RE and working electrode WE. This difference ΔE is amplified with the open - loop gain A(ω) to $\Delta E \cdot A(\omega)$. The internal resistance of the power output stage R_i reduces the amplified open - loop voltage of the output by the amount $I_a \cdot R_j$ if the output is loaded by the cell current I_a. Here R_j is the internal resistance of the output stage R_m is the resistance of a current measuring device R_z is the cell resistance from the counter electrode to the boundary layer R_e is the boundary layer impedance; the drop across it is E_e.

3. Apparatus and Procedure

The amperometric measurements were carried out with a low power potentiostat. The schematic potentiostat was verified with the SIMULINK program (Figure 5).

Commercially available potentiostats tend to be large in size and expensive. They also tend to be laboratory-based and not field-portable and do not, for example, lend themselves to being carried into the back country for on-site measurements. For these reasons, it was desirable to design and build a small, rugged, inexpensive potentiostat to interface with various types of electrochemical probes.

We have designed a potentiostat circuit that accepts an electrical signal, proportional to current flowing through the electrolyte (in the electrochemical cell) and measure the time it takes to charge or discharge a capacitor. In an electrochemical cell, any change in the potential of the cathodic electrode, results in a flow of current in the electrolyte so the potential of the electrode is maintained. The potentiostat has two tasks: to measure the potential difference between working electrode and reference electrode without polarizing the reference electrode, and to compare the potential difference to a preset voltage and force a current through the counter electrode towards the working electrode in order to counteract the difference between preset voltage and existing working electrode potential [3]. The correct connection of the cell is essential for error - free operation of an electrochemical system. As soon as the counter electrode voltage of a potentiostat exceeds 40 V, the voltage may become hazardous to your health. Before disconnecting the cell, set the potentiostat to the stand - by - mode, and connect the reference electrode plug to that of the counter electrode [7].

Reference electrodes have a high source resistance. From this reason, the reference electrode input of the potentiostat always must have a high input resistance. Most potentiostats keep the working electrode on ground potential. The working electrode is not in any case connected to ground: it is virtually kept on ground potential. As the working electrode cable itself has some resistance, potential errors may occur due to the potential drop in the working electrode cable. It is therefore good practice to have two connections at the potentiostat: One for the working electrode potential cable, and another for the current cable. As long as the currents remain below some few

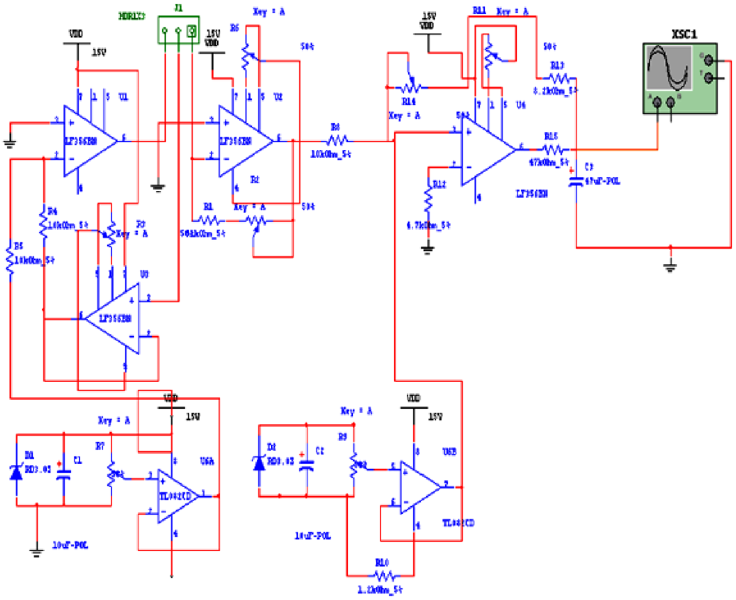

Fig. 5. *The schematic potentiostat*

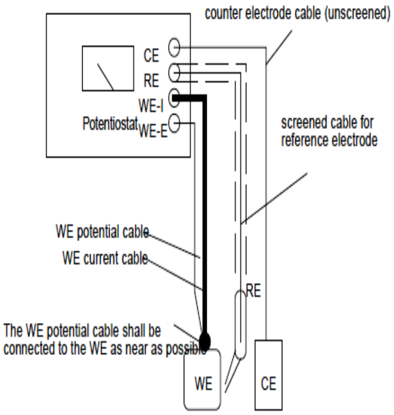

Fig. 6. *The schematic correct connection*

milliamperes, both terminals may be connected at the potentiostat, and only a single wire is used to connect the working electrode (Figure 6).

4. Experimental Determinations

The experimental measurements were accomplished using physical methods of conductivity and amperometric potentiometers investigations. The constructed potentiostat has a good linearity in the nanoampere current range that is relevant for many chemical measurements. This potentiometer has a very low-power consumption, and may easily be adapted to meet the requirements of different electrode-based amperometric sensors. Our aim was to obtain the calibration curve for the potentiostat. It was measured the dependency between the current and frequency (Table 1).

Table 1

The current to frequency dependency

f [Hz]	15	20	40	60
I [nA]	50	65	120	180
f [Hz]	90	120	150	200
I [nA]	270	340	420	620

We processed the experimental data by making use of a TBLCURVE and ORIGIN SOFT. In Figures 7 and 8 there is represented the dependency between the current-to-frequency calibrations curves obtained for the potentiostat.

By processing the experimental data by making use of a TBLCURVE and ORIGIN SOFT there was established the equation of the curve of dependency of the current-to-frequency.

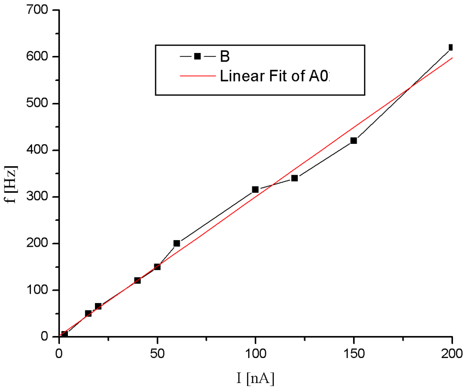

Fig. 7. *The current-to-frequency calibration curve obtained with ORIGIN SOFT*

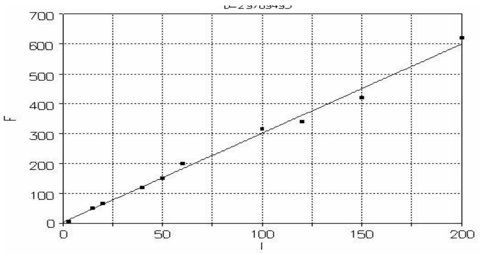

Fig. 8 *The current-to-frequency calibration curve obtained with TBLCURVE SOFT*

The Figures 7, 8 shows that the current-to-frequency transfer function is linear between approximately 4 and 200 nA and extends up to currents of 700 nA. In the linear region, after processing the experimental data, the output frequency there was obtained by the following equation:

$$f_{out} = -2.8472 + 2.9769 \cdot I_{cell}\,, \qquad (1)$$

where, I_{cell} is the electrode current in nA. We find that the zero offset of the converter is 2.8472 nA, and the sensitivity is 2.9769 Hz/nA.

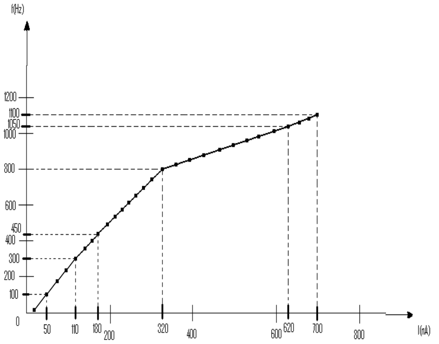

Fig. 9. *The current-to-frequency calibration curve of the potentiostat*

We can see in Figure 9 that the response is non-linear above 200 nA and the calibration curves were consistent and reproducible over the full range tested. In fact, we developed a current-to frequency converter circuit. The above presented potentiostat exhibits good linearity in the current range up to 200 nA when calibrated with highly stable thick-film resistors, with a detection limit of approximately 3 nA. In the embodiment tested, a sensitivity of just over 3 Hz/nA was achieved. The potentiostat was able to control the working electrode potential with respect to the counter electrode with a regulation of better than ±2% under various complex load impedances. The circuit consumes 500 μW of power, achieved through the careful use of low-power CMOS amplifiers in the circuit design, and minimal quiescent current drain, and is therefore suitable for operation from standard 3 V Lithium coin cells.

5. Conclusions

The specific unique qualities of this current-to-frequency converter that make it particularly suited to this type of application are high input impedance, necessary to obtain accurate amperometric measurements and the direct production of a pulsed digital output, compatible with low-voltage CMOS logic gates, using only a few components. We offer this instrument design as a laboratory experiment or special project for more advanced students. Students in advanced analytical and integrated laboratory courses often study electronics and build instruments in order to better understand their design, function, and optimization. Students interested in analytical instrumentation including projects involving portable electrochemical instrumentation, might also find this potentiostat useful. This apparatus has been designed by us for implementing the function of an amperometric potentiostat with a minimum number of components. The simple circuit presented here is solid state, amenable to battery powered operation, and if interfaced to an appropriate electrochemical cell, can be used as a rugged, field-portable sensor system for monitoring environmental contaminants. This particular design may easily be adapted to meet the requirements of different electrode-based amperometric sensors.

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