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DESIGN OF AN EFFICIENT, INEXPENSIVE AND PORTABLE POTENTIOSTAT FOR ELECTROCHEMICAL BIOSENSING APPLICATIONS

S. Gokul[1], S. Rathinavel[2] and E. Velumani[3]
[1,2]Department of Electronics and Instrumentation, Bharathiar University, India
[3]Department of Electronics, PSG College of Arts and Science, India

Abstract
Electrochemistry is a branch of science that deals with electricity and its relationship with corresponding chemical reactions. A potentiostat is an instrument that aids in electrochemical studies. It is employed in various studies like amperometric, potentiometric, and electrochemical impedance spectroscopy. Potentiostat controls an electrochemical cell where the applied potential or current is varied, and chemical reactions related to variations are studied. The findings from the potentiostat help in quantitative and qualitative analysis of the sample of interest. Usually, a conventional potentiostat is priced high and requires a laboratory setup for its working. To make a potentiostat at a low-cost and portable, microcontroller along with operational amplifiers and other electronic components can be used. ARM architecture-based 32-bit microcontroller-STM32 Nucleo-144 board applied in the construction of microcontroller potentiostat. DAC and ADC functions along with the functions of operational amplifiers are implemented in the design and working of the potentiostat. A 32-bit microcontroller is employed due to its high operating speed and wide resolution. The designed potentiostat can be interfaced with an LCD or serial plotter to gather the required data for the analysis. The advantages of microcontroller-based potentiostat are factors relating to cost, portability, and ease of usage.

Keywords:
Potentiostat Design, Electrochemistry, Cyclic Voltammetry, Point-of-Care Device

1. INTRODUCTION

In our daily life, electronic technology plays a crucial role, mostly all the tasks we do either directly or indirectly related to electronic technology. Electronics help in simplifying complex tasks and many applications are made using them. A potentiostat can be designed by a microcontroller. The potentiostat is an analytical instrument used in electrochemical studies. It is connected to an electrochemical cell which is usually a three-electrode system that consists of a working electrode, reference electrode, and a counter electrode. An electrochemical biosensor needs a potentiostat for its working to make it a handheld and point of care device. Even though there is vast research taking place in the field of biosensors, the development of low-cost and point-of-care (POC) diagnostics which has features like portability, acceptable performance, and ease of use is not yet has been achieved its full potential [1]. There are a few proposed microcontroller-based potentiostats that form the basis of this research but they do have their own merits and demerits [2] – [5].

The Microcontroller is needed for two important functions, Digital to Analog conversion (DAC) as the name suggests it converts the digital values to their respective analog values. After performing necessary applications, Then the signal is again converted to digital values using Analog to Digital Conversion (ADC) for the microcontroller to read and process the data. STM32 Nucleo 144 board is used as a processing unit for the development of potentiostat, it is a 32-bit microcontroller that uses ARM architecture for its operation. It has a 12-bit wide DAC and ADC.

In the previous work done by Gabriel N. Meloni [3], potentiostat was designed in Arduino Uno board and the major drawback of the board is that it does not have featured DAC output and PWM output along with integrator function of an operational amplifier is needed for DAC operation and also PWM is of only 8-bit resolution. In this paper, the Arduino board is replaced with an STM32 Nucleo board which has a dedicated DAC and with a higher resolution of 12 bits. Arduino board has 0.0078V or 7.8mV as a potential step whereas the STM32 has 0.00048V or 0.48mV which helps in better signal processing.

Operational amplifiers are an integral part of potentiostat which are used to perform signal processing operations like the current to voltage conversion, comparison of signals, and amplification of signals. The output can be read through personal computers using multiple software like a serial plotter, Embedded workbench, and various specialized software. But they are helpful when the device is used remotely and there may be a need of providing results in the field of testing itself at crucial times. So an LCD interface with the microcontroller has the advantage of providing the output data at the device level itself.

Biosensors can be classified based on working principles as optical, electrochemical, and mass-based [6], [7]. Optical biosensors work based on light absorption and reflection, they are indirect and sensitive to changes, yet they have disadvantages like they are bulky and inefficient in turbid medium [8]. Mass-based biosensors work based on the piezoelectric effect, mechanical stress, use of mechanical oscillations to determine frequencies [9]. Electrochemical biosensors deal with studies that involve a chemical process that is related to the movement of electrons [10]. It consists of an electrochemical cell that generates voltage and current from the chemical reactions or uses electric signals to stimulate the chemical reactions [11].

Electrochemical biosensors are one of the widely used biosensors because of their advantages like low cost, does not require bulk space, ease of usage [12]. Electrochemical cells with electrodes, electrolytes, and potentiostat are the major components of electrochemical analysis. Usage of portable potentiostat eliminates the problem of portability and point of care testing [8].

Cyclic voltammetry (CV), square wave voltammetry, differential pulse voltammetry are the different types of voltammetric studies to study the electrochemical behavior of the samples. For the preliminary research, only cyclic voltammetry technique measurements are developed. In CV, the potential of the is ramped linearly versus time and its corresponding current changes are measured. It is used to study redox reactions, reaction stability, presence of intermediaries, reversibility of reaction, and electron transfer kinetics [13] – [15]. Various cyclic voltammetry experiments can be carried out using portable potentiostat-like measurements of ascorbic acid in orange juice and monitoring redox of ferricyanide [5].

Using handheld biosensors, Preliminary tests can be carried out and the critical samples could be tested using conventional tests that will reduce the workload of laboratories that uses conventional techniques. The testing and logistical issues can be avoided. Tests can be carried out even in rural areas by utilizing the devices in primary health centres as the device can be accessed by a semi-skilled person and manufacturing cost is also viable in developing countries like India. The biosensors can be applied in biological applications which are associated with health and environmental parameters.

2. MATERIALS AND METHODS

2.1 MATERIALS

STM32F746ZG microcontroller, an electrochemical cell with electrodes, LM324 operational amplifiers, LCD, power source, and other passive electronic components. Chemicals such as potassium ferricyanide ($K_3Fe(CN)_6$), potassium chloride (KCL), potassium dihydrogen phosphate (KH_2 PO_4), ascorbic acid (vitamin C), and hydrochloric acid (HCL) are used. Double distilled water is used throughout the experiments.

2.2 SAMPLE PREPARATION

Redox reaction of potassium ferricyanide studied by mixing 20mM $K_3Fe(CN)_6$ and 0.5M of KCL to make a solution, which is prepared fresh and used. Phosphate buffer solution of 2.0 pH is used as a buffer for the determination of ascorbic acid. PBS is prepared before the test and pH is adjusted to the desired range by adding HCL. The ascorbic acid stock solution of 0.1M is freshly prepared and 200 µM concentration is used for voltammetric studies.

2.3 CIRCUIT DESIGN

The working circuit of microcontroller-based potentiostat is given in Figure .1. A microcontroller is the main component of the circuit which is used to control the voltage of the working electrode using DAC output and process back the information from the counter electrode via ADC as input.

DAC output of the microcontroller is fed into an operational amplifier which acts as a summing amplifier. The device potential is controlled using the summing amplifier. The potential window of operation can be altered by changing input voltage and resistance values. By default, the DAC output varies from 0 to 3.3V. For most practical applications, an operating voltage of 2V which is from a range of -1 to 1 is enough. The working electrode is connected to an operational amplifier output whose inputs are reference voltage from the reference electrode and output of summing amplifier output. The cycling of voltage from one level to another causes the current changes in the counter electrode. These currents are very small, which are in a few microamperes range(µA). The current is changed into a voltage signal for microcontrollers to read, a current-voltage converter is used. After further amplification, the signal is fed into the analog input of the microcontroller. ADC operations are performed and the result can be presented to the user in graphical representation using an LCD or serial plotter application.

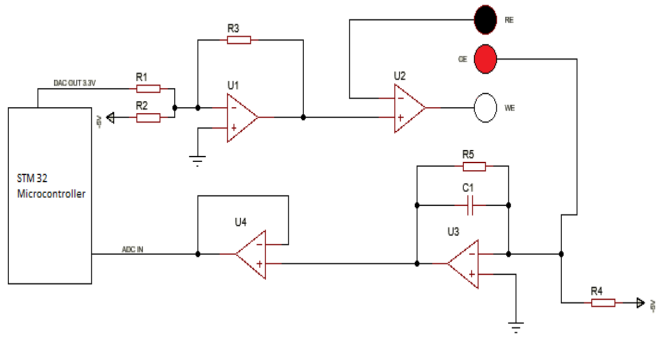


Fig.1. Circuit Diagram of the Proposed Potentiostat

2.4 ELECTROCHEMICAL STUIDES

Electrochemical studies are carried out in conventional type potentiostat and microcontroller-based potentiostat. OrigaFlex-OGF01A potentiostat and the designed potentiostat are used for the same. Glassy carbon electrode (GCE), saturated calomel electrode, and platinum wire electrode are used as working, reference, and counter electrodes respectively. Electrodes are well cleaned and used.

3. RESULTS

3.1 CYCLIC VOLTAMMETRY OF POTASSIUM FERRICYANIDE

The electrochemical behavior of potassium ferricyanide is investigated using cyclic voltammetry. A bare GCE is used for this purpose. Fig.2. represents the cyclic voltammogram of potassium ferricyanide solution with the presence of potassium chloride. From the graph, the appearance of intensive peaks in both the axes of the graph represents the oxidation and reduction reactions.

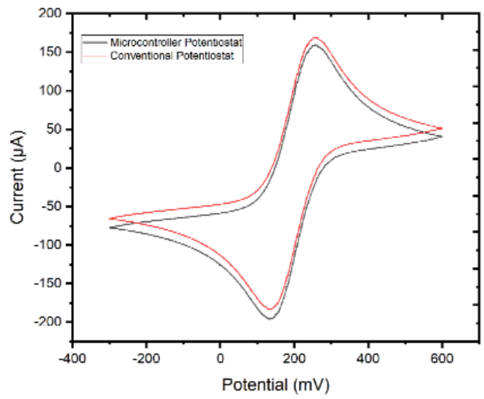


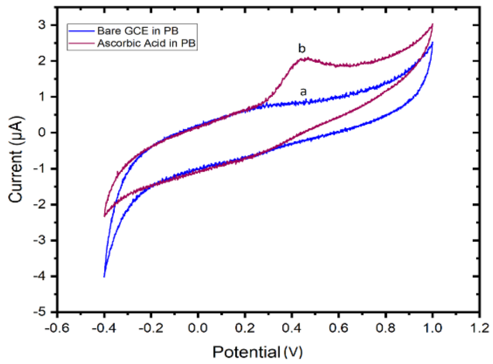
Fig.2. Cyclic Voltammogram of potassium ferricyanide with bare GCE at a scan rate of 50 mV/S

The Eq.(1) represents the reaction occurring at the working electrode. Cyclic voltammogram is done under a nominal scan rate of 50 mV/s. A microcontroller-based potentiostat was able to perform with an acceptable limit in comparison to the conventional with slight variations.

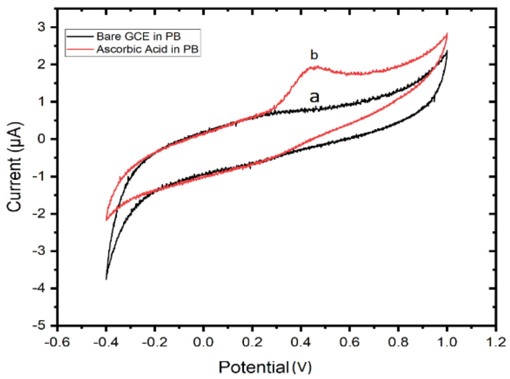
$$Fe(CN)_6^{3-} + e^- \leftrightarrow Fe(CN)_6^{4-} \quad (1)$$

3.2 CYCLIC VOLTAMMETRY OF ASCORBIC ACID

Electrochemical techniques can be employed for the quantitative determination of ascorbic acid in the sample of interest. The analysis is carried out in both types of the potentiostat. Cyclic voltammogram from conventional potentiostat is shown in Fig.3. (a). and from microcontroller potentiostat is shown in Fig.3. (b). Scans are carried out in 50 mV/S in GCE of 2.0 pH PBS as it is the optimum pH range for determination of ascorbic acid from the previous work [16]. From the graphs, [a] represents bare GCE in PBS without ascorbic acid and there are no presence peaks in the voltammogram, and [b] represents a solution with the presence of ascorbic acid with a concentration of 200 μM. The peak is present near +470 mV indicates the presence of ascorbic acid in the sample of analysis. The peak current is around 2.10 μA from conventional potentiostat and 1.97 μA by microcontroller potentiostat.



(a) without ascorbic acid (b) 200 μM ascorbic acid



(a) without ascorbic acid (b) 200 μM ascorbic acid

Fig.3. Cyclic Voltammograms for determination of ascorbic acid

Oxidative current peak is present, and reduction current peak is absent shows the irreversible oxidation of ascorbic acid to dehydroascorbic acid. The oxidation (Eq.2.) reaction that occurs at the working electrode is due to surface adsorption [17].

$$C_6H_8O_6 \rightarrow C_6H_6O_6 + 2H^+ + 2e^- \quad (2)$$

3.3 COMPARATIVE STUDY

The performance of the designed microcontroller-based potentiostat is studied with a conventional potentiostat. From the Fig.4 comparison study of voltammograms recorded are plotted with each other. From the graph, it is clear that the designed potentiostat matches the performance of the conventional one. Variations of current measurement from Table.1 which are less than 5% understood to be within acceptable limits.

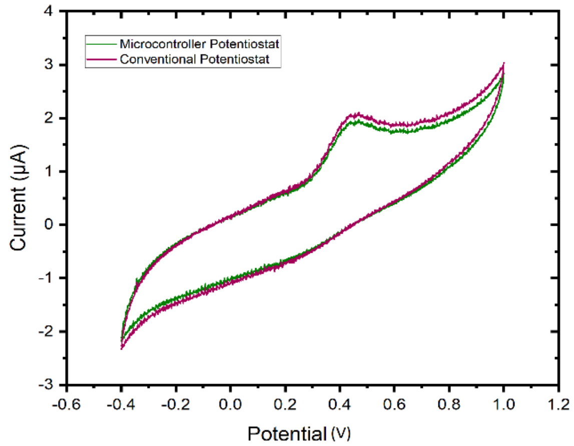


Fig.4. Cyclic voltammogram of 200 μM concentration of ascorbic acid in GCE.

Table.1. Parameters comparison

Potentiostat	Applied potential range (V)	Scan rate (mV/s)	Current (μA)
Conventional	-0.4 to 1.0	50	2.10
Microcontroller	-0.4 to 1.0	50	1.97

4. CONCLUSION

A microcontroller-based potentiostat is designed and tested. It is cost-effective and can be used as a portable device with acceptable performance as an electrochemical biosensor. From the studies, it can be concluded it is as efficient as conventional potentiostat with an efficiency of more than 95%. Though the ascorbic acid is sensed with bare GCE, the peak current of the voltammogram is very less which emphasizes the need for electrode modification to overcome the shortcomings. Considering the advantages, it can be a greater substitute for conventional ones. Biosensors that uses microcontroller-based potentiostat can serve as rejection window and help in reducing the laboratory tests by serving as a preliminary test device, the critical results from the analyses samples can be sent to further analysis for confirmation studies.

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