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"EduPotStat": Construction and testing of a low cost potentiostat

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Abstract:
In this work we developed a low cost potentiostat to monitor redox processes using open source software and hardware for undergraduate laboratories in the developing countries. The developed system consists of three main modules namely user interface, triangular voltage generator, and current to voltage converter. Arduino Uno, 12-bit digital to analog converter and nine operational amplifiers were used to construct the proposed hardware. It operates in voltage range -2.5 V to +2.5 V and measure current in the range of ± 25 μA -0.025 A with 10 nA resolution and 1 mV DC-potential resolution for the cyclic voltammetry measurements. The performance of this system is compared with a commercially available potentiostat using $K_3Fe(CN)_6$ solutions. The three-electrode system reported here is screen-printed electrodes with aqueous KCl as the electrolyte. Results are in good agreement with commercially available research grade potentiostat. Overall cost for developed system is around $50 which make possible to use in undergraduate education.

Key Word*:Cyclic voltammetry; Digital to analog conversion; Electrochemical measurements; Potentiostat; Three-electrode system*

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I. Introduction

Commercially available potentiostats, often cost upwards of $5000/$6000 per channel or $1,000 for a model with limited functionality[1]. In addition, these commercial instruments are typically impractical to use in field researches. Therefore, teaching laboratories in the fields of both electronics and electrochemistry, and developing teaching centers that cannot afford a commercial device are faced with more difficulty. While a low cost potentiostat device cannot rival the quality and capabilities of research-grade potentiostats, many of the features of top-of-the-line commercial instruments are unnecessary for environmental or public health applications and portable applications[1,2,3]. However, high school students or university students will be benefitted by inexpensive potentiostats which are used for teaching purposes. Therefore, desirable to design and assemble a potentiostat which is easy in operation as well as economically cheap.

However, in order to reduce price, size and complexity, custom made potententiostats can be implemented with limited functionality compared to the commercially available high grade potentiostats. In the review of literature there were several low cost, open source, microcontroller unit (MCU) based, miniature potentiostats have been described over the last decade[1,3–12]. When the history of potentiostat is considered, the first research paper about MCU based potentiostat was published by Vittal and Russell[3]in 2006 for cyclic voltammetry. This is the first open source design of an inexpensive potentiostat that is field ready for long-term chronoamperometry. PIC18F452 microcontroller was used in this potentiostat and there are some limitations associated with design. More recent open-source potentiostat development has focused on miniature potentiostats, often with implantation in mind [1, 4, 5,7, 8, 12–16]. These devices offer additional options than Vttal and Russel's with minimizing drawbacks. A LabView based potentiostat was developed by Avdikos which is not an open source platform[9]. But none of the above developed systems are not commercially available.

However, the "CheapStat: An Open-Source, "Do-It-Yourself"Potentiostat for Analytical and Educational Applications" was built for under $60 (or < $80)[1,5]. This device is commercially available and supports multiple measurements mode such as cyclic, square wave, linear sweep stripping voltammetry over the potential range -990 mV to 990 mV. But this potential range is not enough for some experiments. Other limitations associated with this potentiostat are having onboard LCD display and input parameters (Frequency, starting voltage, end voltage, scan rate) must be set through that limited onboard LCD display and 5-way joystick. Therefore, that device is lack of user-friendliness.

The system developed in this work use open source hardware and software. It is a low cost three-electrode potentiostat for electrochemistry measurements capable to run cyclic voltammetry measurements. The system consists of three main modules namely a user interface, a triangular voltage generator, and a current to voltage converter. User inputs of scanning voltage range and scanning rate can be input through the user interface. Triangular voltage generator consists of four sub circuits such as ATmega328p microcontroller based 12-bit step counter, digital to analog converter (MCP 4725 12-bit DAC), difference amplifier and inverting summing amplifier. This module outputs a triangular voltage in the range of -2.5 V to +2.5 V at a user given rate where it connects to the counter electrode of the three-electrode system.

II. Material And Methods

The potentiostat has two main tasks: The first task is to measure the potential difference between the working electrode (WE) and the reference electrode without polarizing the reference electrode. The second task is to compare the potential difference to a preset voltage and force a current through the counter electrode (CE) towards the WE in order to counteract the difference between preset voltage and existing WE potential. To perform cyclic voltammetry, a triangular voltage is applied to the WE. During the voltage waveform applied time electron transfer occurs withinthe electrochemical cell; this current is measured at the WE and recorded for analysis.

Basic Potentiostat circuit

A basic potentiostat circuit is presented in Fig. 1 The reference electrode (RE) is connected to the "OP Amp B" which is a voltage follower and has near infinite input resistant, therefore no significant current transfer can occur at this electrode. The voltage-follower circuit helps in maintaining a constant potential at the RE without drawing much current. Input triangular voltage waveform is applied to the electro chemical cell at the CE respect to the RE using the current buffer "Op Amp A" (control amplifier). The input of the current buffer is isolated from the output, therefore the current at the output of the op amp is not limited by the input current and is capable of providing infinite current (effectively infinite, practically 1 A) to electro chemical system which is needed to undergo chemical reactions. The current flow between the CE and the WE.

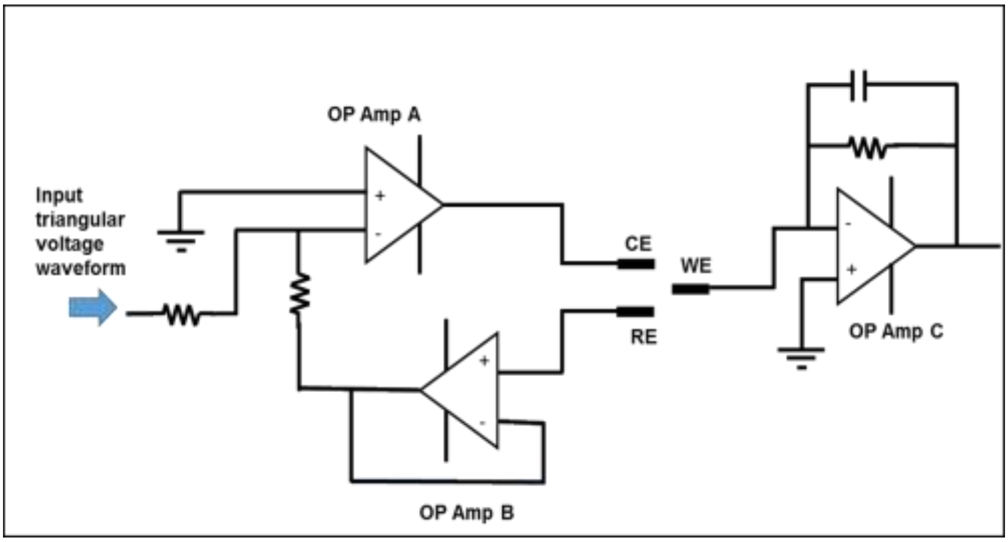

Fig. 1. Basic Potentiostat Circuit

By applying the voltage waveform, the potential difference is controlled between the WE and the CE and also the potential difference is measured between the WE and the RE. Because the WE is kept fixed stable potential (pseudo ground) by controlling the polarization of the CE, the potential difference between the WE and the RE is controlled all the time. The potential difference between the WE and the RE will be equal to the applied triangular voltage waveform. This configuration allows the potential across the electrochemical interface at the WE to be controlled with respect to the RE. For a potentiostat to operate correctly, the WE must maintain a zero potential. Therefore, the WE is connected to the inverting terminal of the "Op Amp C" while the non-inverting terminal is connected to the ground. In this configuration virtual ground creates at the WE and that also creates a negative voltage across the measuring resistor at the "Op Amp C". The current generated from the electrochemical cell is forced to flow through the resistor of "Op Amp C". When the resistor value is known and the voltage across the resistor is measured, can calculate the current through the cell. In this case, “Op Amp C” acts as a current to voltage converter.

Electronics in Potentiostat design

The block diagram of the EduPotStat is presented in Fig. 2 The developed system consists of four distinct parts: (i) Microcontroller Unit (MCU – ATmega328p), which serve as a central processing unit, generates the triangular waveform in digitally, measure the voltages and running all other functions, (ii) 12 bit Digital to Analog Converter (DAC -MCP 4725 breakout board, control it via I2C), which converts the digitally generate triangular waveform to analog signal, (iii) external circuit (consist of operational amplifiers, resistors, capacitors..etc), which provides the core of the potentiostat and interface between the MCU and the electrodes, (iv) personal computer, which provides the user interface to control the potentiostat from the GUI.

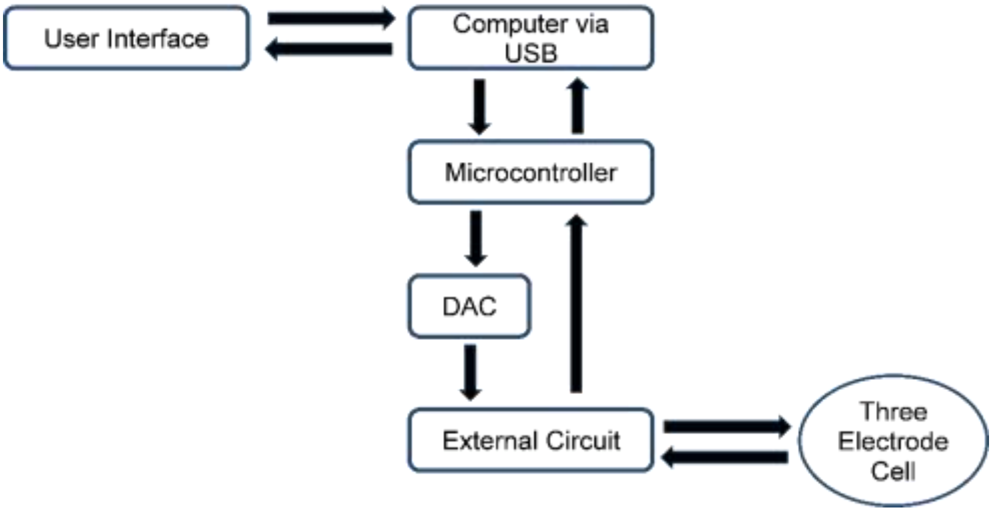

Fig. 2. Block diagram of the EduPotStat

The schematic of the developed EduPotStat is presented in Fig. 3 MCU programmed to generate a triangular waveform as digital form according to user input using a 12 bit up-down counter. The output of the MCU’s digital signal will convert to analog triangular voltage waveform by DAC. The output of the DAC is fed to the external circuit through a voltage follower (Op-1, Fig. 3). The voltage follower circuit is used to isolate the external circuit from the MCU with DAC. But the output of the DAC is unipolar (between 0 V and +5 V Fig. 4); to change the output voltage to bipolar (between -2.5 V and +2.5 V, Fig. 5) an op amp difference amplifier circuit (Op-2 and Op-3, Fig. 3) is used as a level shifter.

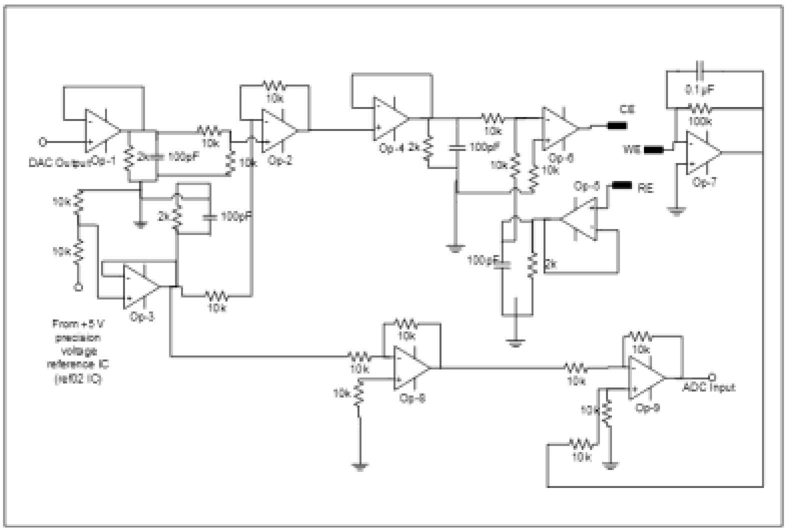

Fig. 3. Schematic diagram for the external circuit of the developed potentiostat. All Op-Amps are powered with ± 12 V power supply. (CE – Counter Electrode, WE – Working Electrode, RE – Reference Electrode)

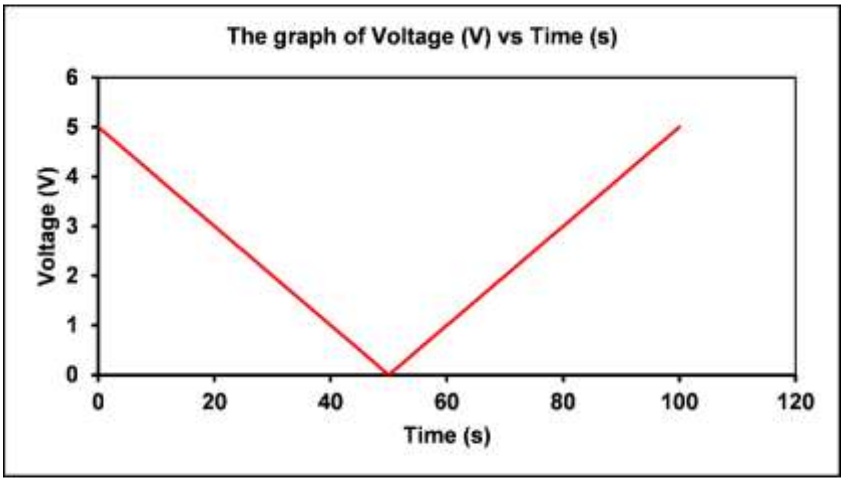

Fig. 4. Output voltage waveform of the Digital to Analog Converter

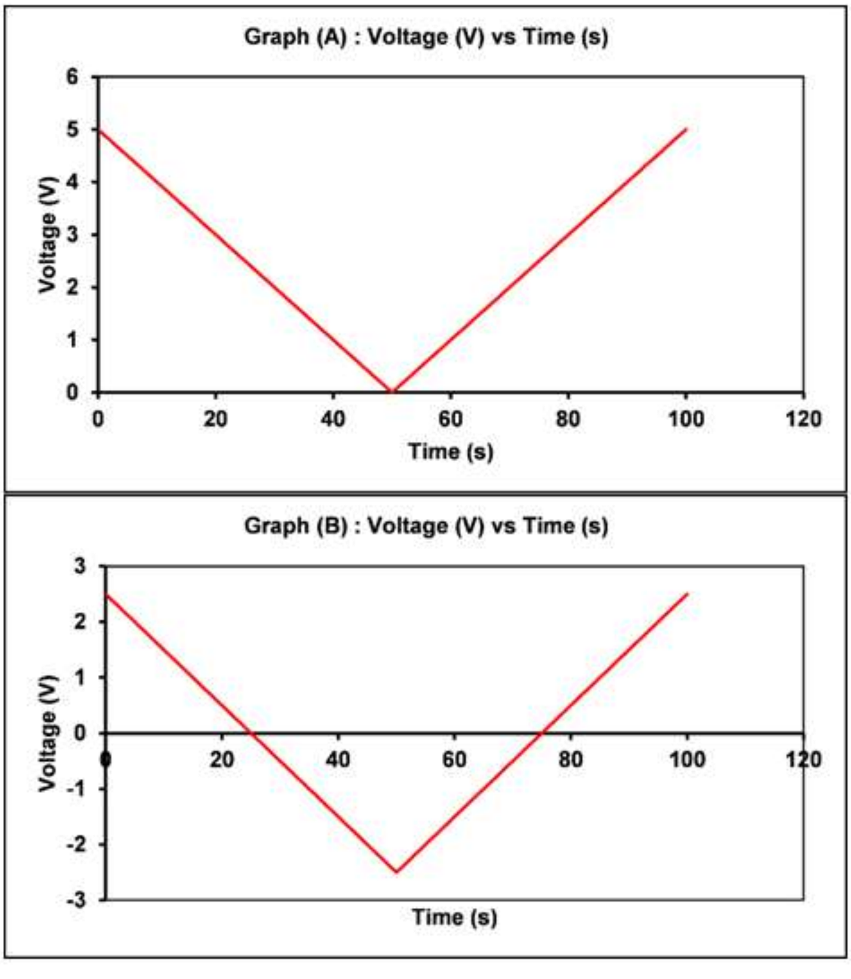

Fig. 5. Graph (A) - Output wave form at the DAC; Graph (B) - Output of the level shifted difference amplifier

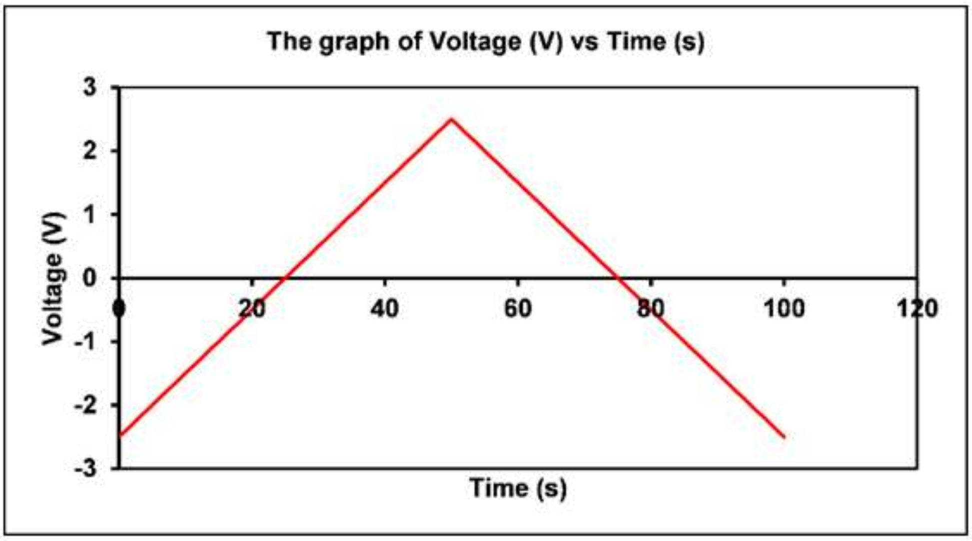

Fig.6. Triangular Waveform at the working electrode which is used to perform cyclic voltammetry

Another two-voltage follower circuit (Op-4 and Op-5, Fig. 3) is used in an external circuit. The RE is connected to the non-inverting terminal of a voltage follower circuit (Op-5, Fig. 3). The voltage-follower circuit helps in maintaining a constant potential at the RE without drawing much current (RE will be polarized when current passes through the RE and cannot maintain a constant potential. Voltage follower circuit will prevent that phenomena.) An inverting summing amplifier is inserted between the level shifted voltage and CE; the inverting summing amplifier (Op-6, Fig. 3) is fed the level shifted voltage to the electro chemical cell respect to the RE. The WE is connected to the inverting terminal of a current-to-voltage converter (Op-7, Fig. 3); feedback resistor of the current to voltage converter will produces a voltage equivalent of the electrochemical current at the output of the voltage converter. The electrochemical current, now converted to a voltage, is level-shifted usinganother difference amplifier circuit (Op-8, Op-9 Fig. 3) and attenuated/amplified to bring the voltage into the 0 V to ± 5 V range which can readable at the Analog to Digital Converter (ADC) in MCU. Because the inbuilt 10-bit ADC of the MCU can read voltage between 0 V and +5 V. ATmega 328p microcontroller uses its own voltage references. But they are not very precise. Limit of the analog measurement accuracy depends on the used voltage reference. Here, microcontroller used allows to providing a substitute for its default voltage reference byproviding an Analog Reference (AREF) input. Therefore, an external voltage reference (REF-02, LINEAR TECHNOLOGY) (Fig. 7) was used to improve the accuracy of the analog voltage measurements. The same external voltage reference was used to supply voltage to DAC to get accurate analog voltage waveform as well. Microcontroller was programmed such that the user can set initial voltage and peak voltage of the required triangular waveform and also can select the scan rate using the Arduino Serial Monitor.

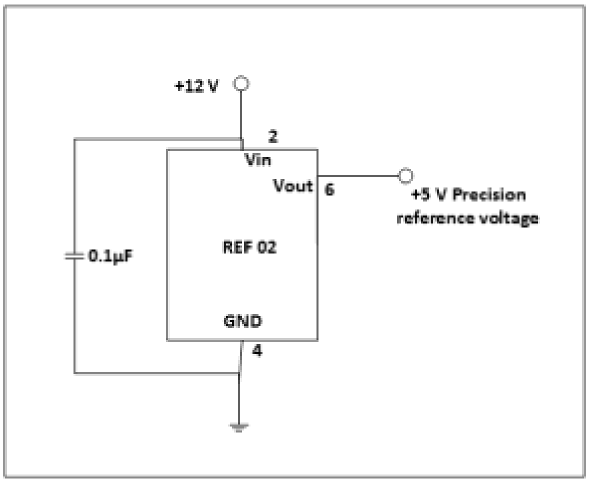

Fig. 7. External voltage reference circuit

Software design

Arduino IDE used to program the MCU where the program consists of three parts: (i) providing user input to control the EduPotStat (ii) generating a voltage waveform to the analog circuit (iii) read and record input voltages to the electrochemical cell and the current received at the ADC as a voltage which then converted to current. User can connect the EduPotStat to one of the PC's USB ports. Then the user will be guided for required user inputs when opening the Arduino IDE serial monitor.

Electrodes

Fig. 8. Pine screen printed electrode. (a)-Counter Electrode,(b)-Working Electrode,(c)-Reference Electrode

In this work "Pine Screen Printed Electrodes" were used as three electrode system[17,18]. These offer some advantages over traditional electrodes in the areas of cost, solution volume, and operating temperature.

System testing

The EduPotStat's performance was compared with an Autolab PGSTAT204 potentiostat/galvanostat which is commercially available. For testing the potentiostat, cyclic voltamagmogram was recorded for 1 mol/dm^3 solution of potassium ferricyanide in 0.1 mol/dm^3 electrolyte solution of potassium chloride. A beaker (50 mL) was used as the electrochemical cell where three electrodes were set up. The current (i) vs. voltage (v) was recorded for -0.7 V as the starting voltage and 1 V as the switching voltage. The experiment was conducted using two scan rates 100 mV/s and 200 mV/s.

III. Result

The cyclic voltammetry for the test species Fe^{2+}/Fe^{3+} has the theoretically predicted shape as a reversible redox couple. In this study $K_3[Fe(CN)_6]$ is used to test the EduPotStat due to the water solubility of the redox couple. Here, commonly used internal standard, ferrocene was not used due to the water insolubility of the compound. Though, the expected redox Fe^{2+}/Fe^{3+} couple of $K_3[Fe(CN)_6]$ is not reversible to the limits of ferrocene it is qualitatively sufficient to test the system. The cyclic voltamagmogram was recorded using EduPotStat and Autolab potentiometers for the same solution containing $K_3[Fe(CN)_6]$ and KCl. The CV recorded for using 100 mV/s and 200 mV/s scan rates are given in the following Figures 09 and 10 respectively. The reversibility of the redox couple can be evaluated by calculating the ratio between anodic peak current and anodic peak current as well as the difference between anodic and cathodic peak potentials.

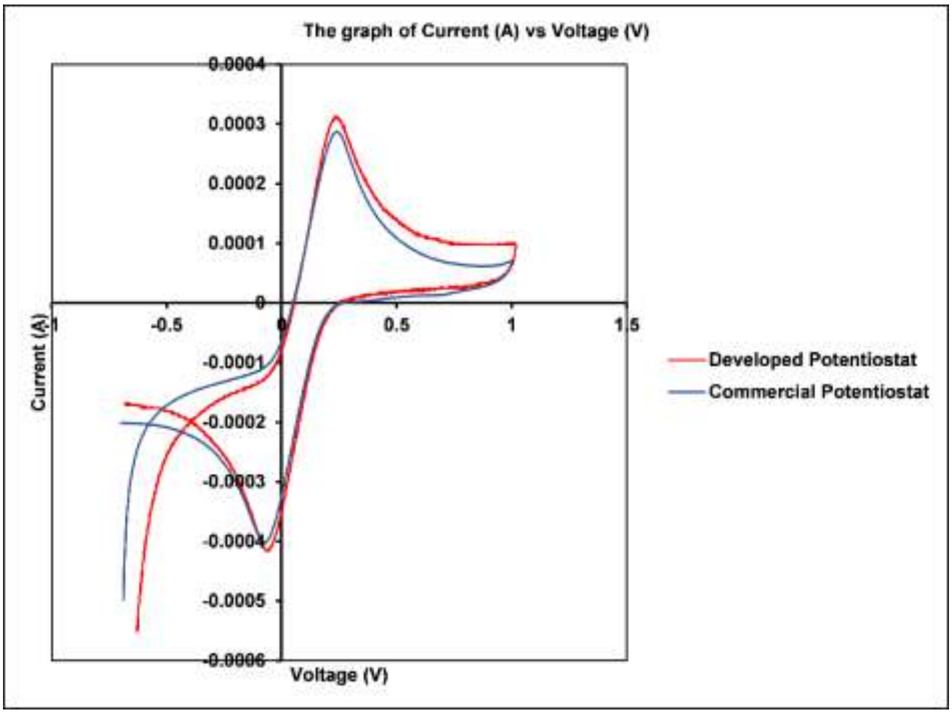

Fig. 9. Cyclic voltammogram for 1 M potassium ferricyanide solution for developed CV system and commercial potentiostat with 0.100 V/s scan rate; Blue colour:Commercial potentiostat, Red colour: developed potentiostat.

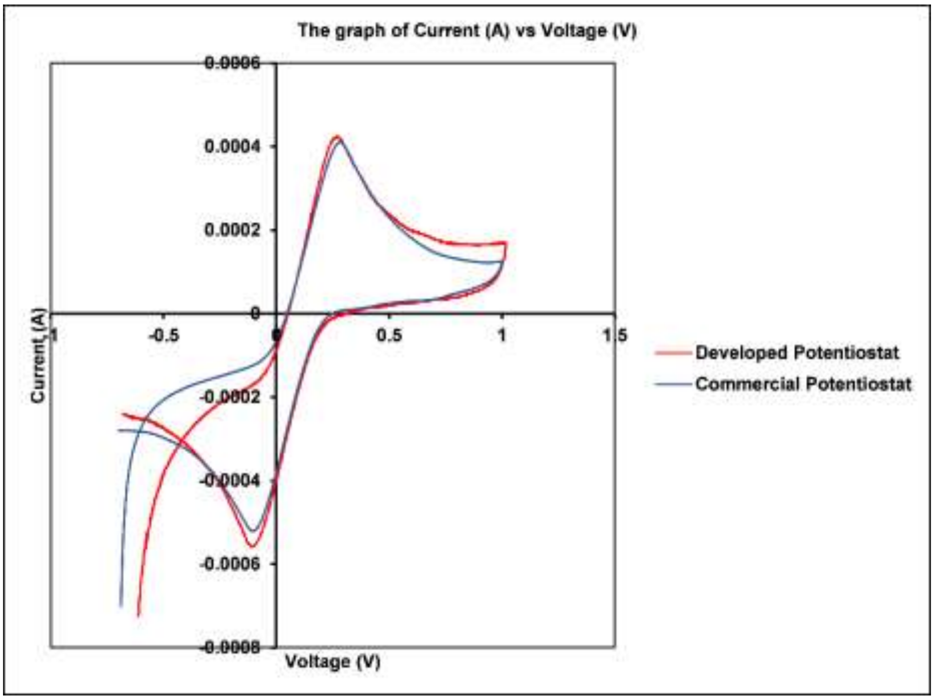

Fig. 10. Cyclic voltammogram for 1 M potassium ferricyanide solution for developed CV system and commercial potentiostat with 0.200 V/s scan rate; Blue colour: Commercial potentiostat, Red colour:developed potentiostat.

Criteria for reversibility are;

$$i_{pc} = i_{pa} \tag{1}$$

$\Delta E_p = \left(E_{pa} - E_{pc}\right) = 0.0592 / n$; Where n is the number of electrons in reaction (2)

Furthermore, the potential of the redox couple can be given as,

$$E_{1/2} = \left(E_{pa} - E_{pc}\right)/2 \tag{3}$$

Table 01: Comparison of redox parameters for the EduPotStat and commercially available Autolab potentiometers for 0.1 V/s scan rate.

	E1/2 (mV)	i_{pa}/i_{pc}	$\lvert E_{pc} - E_{pa} \rvert$ (mV)
EduPotStat	86.79	0.750	297.81
AutoLab	81.05	0.717	309.3

According to Table 01, the $E_{1/2}$ values obtained for the Fe^{2+}/Fe^{3+} redox couples are 86.79 mV and 81.05 mV for the EduPotStat and Autolab respectively. Furthermore, the ratios between anodic and cathodic peak currents are 0.750 (EduPotStat) and 0.717 (AutoLab). Therefore, the system tested in this study is in good agreement with a commercially available CV systems.

When constructing the system, TL074 IC and 741 IC were used for the external circuit because they have high-Input Impedance, low power consumption, wide common-mode and differential voltage ranges, low Input bias and offset currents. The analog circuit is the heart of the potentiostat. Where the EduPotStat supports only for cyclic voltammetry currently. But other operation modes (linear sweep, stripping, square wave voltammetry) can be added with simple microcontroller program algorithms. And also above mentioned operation range can be expanded with simple hardware adjustments. We noted that different power supplies produce slightly different outputs. This is an issue that arose which affected the accuracy of the resulting current since all data is scaled proportionally to Vcc of the DAC. Therefore, a REF-02 (LINEAR TECHNOLOGY) precision 5 V voltage reference was used to improve the accuracy of the analog voltage measurements.

The constructed system can operate voltage range between -2.5 V to 2.5 V, while user can select desire scan rate. Also, the proposed light weight system can construct with low budget. Therefore, this EduPotStat is very field portable and can be used in undergraduate laboratory experiments and analytical applications in developing countries.

IV. Conclusion

In this work we presented that the design of a low cost three electrode potentiostat which operates voltage range in the -2.5 V to +2.5 V for cyclic voltammetry applications with uccessful scanning in both positive and negative voltages. This allows to measure current between ± 0.000025 A -0.025 A ranges with 10 nA resolution and 1 mV DC-potential resolution for voltage measurments with low noise. Test results were good agreement with the commercially available potentiostat. The simple design, construction, easy to operate, low cost (< $50), low power consumption, field portable and good performance are the advantages of the instrumentation. The next steps include creating a graphical user interface to control the device and optimize the potentiostat for provide multiple techniques.

Acknowledgment

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