DEVELOPMENT OF A RECORDING SYSTEM FOR ELECTROCHEMICAL SIGNAL FROM VOLTAMMETRY

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Watcharin Permwong

Researcher

บทคัดย่อ

เรื่อง : การพัฒนาระบบบันทึกสัญญาณทางเคมีไฟฟ้าจากโวลแทมเมตรี

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คำสำคัญ : เคมีไฟฟ้าวิเคราะห์, ไซคลิกโวลแทมเมตรี, โพเทนซิออสแตท, ไมโครคอนโทรลเลอร์

ในงานวิจัยนี้ โพเทนซิออสแตท (Potentiostat) ได้ถูกออกแบบและพัฒนาให้มีต้นทุนที่ต่ำลงและขนาดกระทัดรัดเมื่อเปรียบเทียบกับโพเทนซิออสแตทที่ใช้กันโดยทั่วไป ดังนั้นไมโครคอนโทรลเลอร์ชนิด เอสทีเอ็ม 32 นิวคลีโอ 32 ถูกนำมาใช้เป็นอุปกรณ์ควบคุมการทำงานเพื่อบรรลุตามวัตถุประสงค์และแอพลิเคชันได้ถูกออกแบบเพื่อใช้เป็นระบบสำหรับบันทึกข้อมูล แสดงผลสัญญาณที่ได้จากการทดลองและใช้งานสำหรับกำหนดตัวแปรต่าง ๆ ที่ใช้ในการทดลอง ผลการพัฒนาแสดงให้เห็นว่าต้นทุนที่ใช้ในการพัฒนาโพเทนซิออสแตทและแอพลิเคชันนั้นค่อนข้างถูกและอุปกรณ์มีขนาดเล็กลง อุปกรณ์สามารถป้อนแรงดันไฟฟ้าสำหรับปฏิกิริยาในระบบเคมีไฟฟ้าได้ในช่วง -2 โวลล์ ถึง +2 โวลล์ ด้วยความละเอียดสูงสุด 1 มิลลิโวลล์ กระแสไฟฟ้าสูงสุดที่อุปกรณ์สามารถตรวจวัดได้คือ -0.25 มิลลิแอมแปร์สำหรับกระแสไฟฟ้าลบ และ 0.25 มิลลิแอมแปร์ สำหรับกระแสไฟฟ้าบวก และกระแสไฟฟ้าต่ำสุดที่อุปกรณ์สามารถตรวจวัดได้คือ 2 ไมโครแอมแปร์ แสดงให้เห็นว่าอุปกรณ์มีค่าการตอบสนอง มีเสถียรภาพ และความถูกต้องในการวัดที่ค่อนข้างน่าพอใจและสัญญาณที่ได้จากการทดลองถูกแสดงผลแบบเรียลไทม์ (Realtime) บนสมาร์ทโฟน

ABSTRACT

TITLE : DEVELOPMENT OF A RECORDING SYSTEM FOR ELECTROCHEMICAL SIGNAL FROM VOLTAMMETRY

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DEGREE : MASTER OF SCIENCE

MAJOR : PHYSICS

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KEYWORDS : ELECTROCHEMICAL ANALYSIS, CYCLIC VOLTAMMETRY POTENTIOSTAT, MICROCONTROLLER

This study aimed to reduce the production cost of a potentiostat and minimize its size compared to conventional devices. A STM32 Nucleo32 was used as the main controller unit to achieve the purpose of the study. Additionally, a smartphone application in was created to record data, display an experimental signal and control the parameters of the experiment. It was found that the production cost of the developed potentiostat and the smartphone application was quite cheap while its size remained compact. In term of its usage, this device can apply voltage to electrochemical systems in the range of -2 to 2 VDC with 1 mV resolution. The measurement of the maximum current can proceed -0.25 mA on its negative side and 0.25 mA on its positive side. The lowest current detected was 2 μA. The developed potentiostat presented satisfactory results for sensitivity, stability and accuracy and can be used with a smartphone for real-time measurement.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (CONTINUED)

LIST OF FIGURES (CONTINUED)

CHAPTER 1
INTRODUCTION

In the 21st century, science and technology development are mainly altering the way of people lives, connect, communicate and transact, with deep effect on economic development. Moreover, science and technology are key drivers to the economic development because technological and scientific revolutions underpin economic advances, improvements in health systems, and infrastructure [1]. Also, in education, science and technology have been encourage as one of the main subjects for teaching and learning at all level of student. One of the methods that using for studying science and technology is the design of scientific experiments and the development of equipment for experimenting with students themselves. Therefore, in the recent years, there are many research developments about scientific instruments that do not require advance technology in the design. The most common purpose for research is to provide researchers the assessable instrument that good efficiency, low cost and more compact.

Electrochemistry is one of the major in chemistry which involves the relation of the electrical and the chemical reaction. The principle of electrochemistry has always been applied in studying and researching of the various chemical properties. The use of electrochemistry in the analytical chemistry such as the determination of amount or concentration of substance was called in a specific name that electroanalytical chemistry or electrochemical analysis. The analytical method of electrochemical analysis is related to the measurement of electrical response affected by chemical reaction [2].

One of the interesting sub techniques in the electrochemical analysis is cyclic voltammetry. The analytical method of this technique is detecting current from a chemical reaction occurred from stimulating with an electrical potential in a cycle form. Cyclic voltammetry was used to study an electrochemical process under various conditions such as detection of the intermediate of the redox reaction, The reverse ability of redox reaction, determination of electron saturation within the system and determination of diffusion coefficients of various substances, etc. [3]. Therefore, cyclic voltammetric technique is very useful in the development of electrochemical research.

There are three main components in electrochemical analysis system which consist of electrolyte, electrodes and the electrical signal detection device [4]. In general, the measurement device is called a potentiostat. The potentiostat is very important for electrochemical analysis. It was used to control the voltage between a working electrode and a reference electrode and detect the electrical current signal that occurred from electrochemical reaction [3]. Because of the electrical signal from electrochemical reaction is relatively low and have a lot of noise, so the potentiostat must have high efficiency and high stability. For this reason, it results in the price of potentiostat is quite expensive. The cost barrier of potentiostat is one of a limitation in the development of an electrochemical research. Therefore, the electrochemical research will be developed and more widespread if the price problem is resolved.

In this scope, the potentiostat used for cyclic voltammetric technique will be designed and constructed by using a microcontroller as a main controller unit. The recording system will be developed in form of application on smartphone. Bluetooth signal will be used as a communication protocol.

1.1 Cyclic voltammetry

Cyclic voltammetry (CV) is possibly the most multipurpose electroanalytical technique for the study of electroactive species. Its versatility combined with ease of measurement has resulted in extensive use of CV in the fields of electrochemistry, inorganic chemistry, organic chemistry, and biochemistry. Cyclic voltammetry is often the first experiment performed in an electrochemical study of a compound, a biological material, or an electrode surface. The effectiveness of CV results from its capability for rapidly observing the redox behavior over a wide potential range. The resulting voltammogram is analogous to a conventional spectrum in that it conveys information as a function of an energy scan [5].

CV consists of cycling the potential of an electrode, which is immersed in an unstirred solution, and measuring the resulting current. The potential of this working electrode (WE) is controlled versus a reference electrode (RE), normally used a saturated calomel electrode (SCE) or a silver/silver chloride electrode (Ag/AgCl). The controlling potential which is applied across these two electrodes can be considered an excitation signal. The excitation signal for CV is a linear potential scan with a triangular waveform as shown in Figure1.1

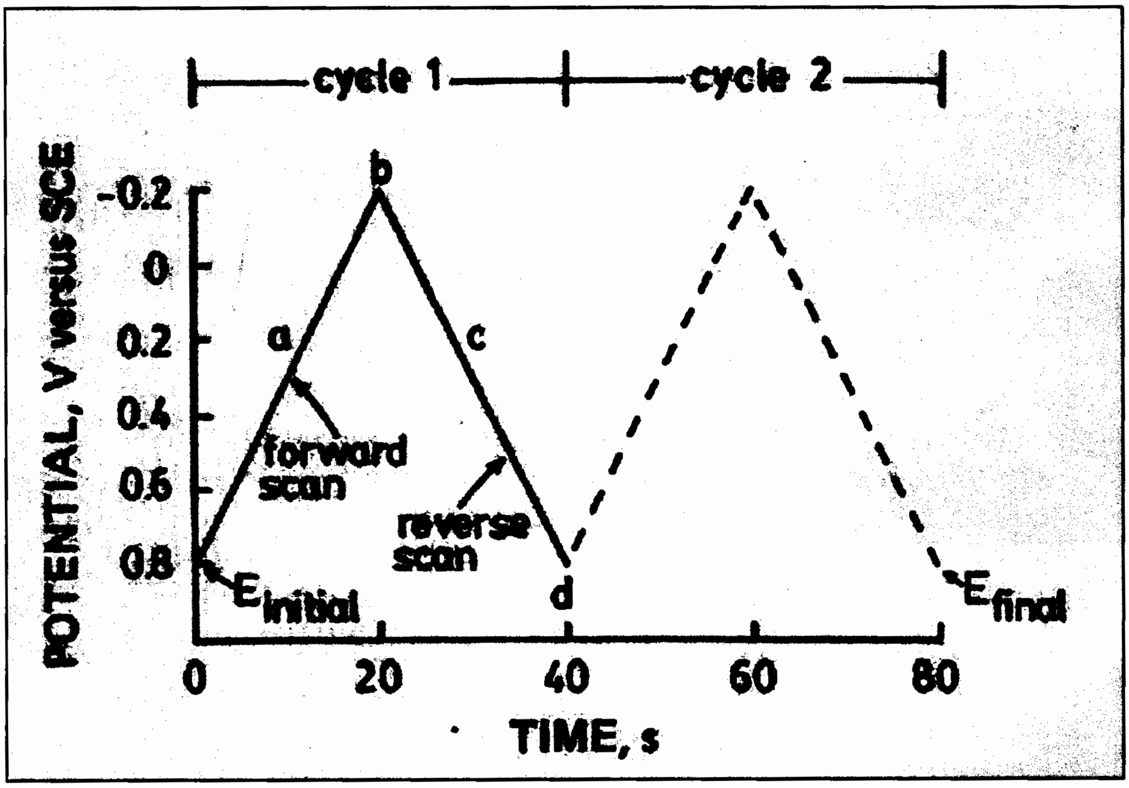

Figure 1.1 Excitation signal for cyclic voltammetry a triangular potential waveform with initial potential at 0.8 V and switching potential at -0.2 V versus RE [5]

The excitation signal sweeps the potential of the electrode between two values, sometimes called the initial voltage and the switching voltage. The potential is firstly scanned negatively from +0.8V to -0.2V versus RE at which point the scan direction is reversed, causing a positive scan back to the original potential of +0.8V. The slope of signal indicates the scan rate value.

A cyclic voltammogram is obtained by measuring the current at the counter electrode (CE) meanwhile the potential scan. The voltammogram is a display of current (vertical axis) versus potential (horizontal axis). A typical cyclic voltammogram is shown in Figure 1.2 which using potassium ferricyanide/ferrocyanide ($K_4fe(CN)_6$) as a redox4 couple.

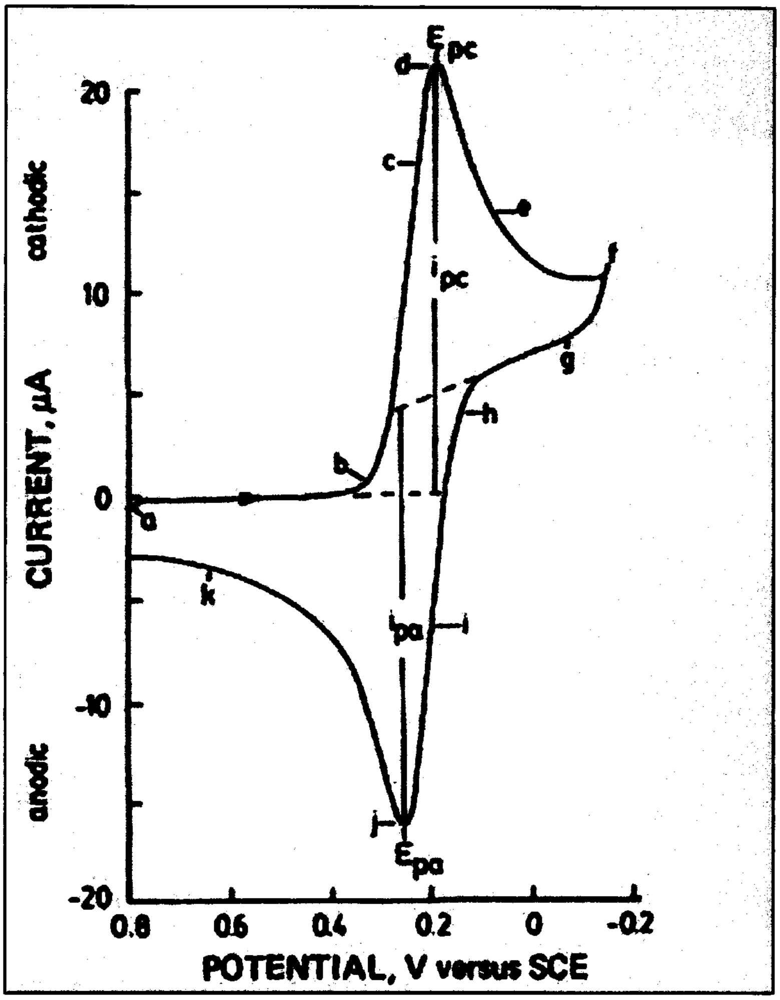

Figure 1.2 A typical cyclic voltammogram [5]

Figure 1.2 shows the initial voltage was set at 0.8 V and applied at "a", label in figure 1.2 and the switching voltage was set at -0.2V. When the electrode is switched on, the potential is scanned negatively, called forward scan. When the potential is sufficiently negative to reduce the potassium ferricyanide (K3Fe(CN)6), cathodic current is occurred at "b" due to the electrode process as follows:

$$Fe(CN)_6^{3-} + e^- \longrightarrow Fe(CN)_6^{4-} \quad (1.1)$$

The electrode is now a sufficiently strong reductant. The cathodic current increases rapidly from "b" to "d" until the concentration of the potassium ferricyanide at the electrode surface is substantially diminished, causing the current to peak "d". The current then decays from "d" to "g" as the solution surrounding the electrode is depleted of the potassium ferricyanide due to its electrolytic conversion to the potassium ferrocyanide ($K_3Fe(CN)_6$). The scan direction is switched to positive at "f" for the reverse scan. The potential is still sufficiently negative to reduce potassium ferricyanide, so cathodic current continues even though the potential is now scanning in the positive direction. When the electrode becomes a sufficiently strong oxidant, potassium ferrocyanide can now be oxidized by the electrode process as follows:

$$Fe(CN)_6^{4-} \longrightarrow Fe(CN)_6^{3-} + e^- \quad (1.2)$$

The anodic current rapidly increases, from "i" to "j" until the surface concentration of potassium ferrocyanide is diminished, causing the current to peak "j". The current then decays from "j" to "k" as the solution surrounding the electrode is depleted potassium ferrocyanide. The first cycle is completed when the potential reaches initial voltage. Now, the cyclic voltammogram is obtained.

The important parameters of a cyclic voltammogram are the magnitudes of the anodic peak current i_{pa} and cathodic peak current i_{pc}, and the anodic peak potential E_{pa} and cathodic peak potential E_{pc}. These parameters are labeled in Figure 1.2 A redox couple in which both species rapidly exchange electrons with the working electrode is termed an electrochemically reversible couple. The formal reduction potential (E°) for a reversible couple is centered between E_{pa} and E_{pc}.

$$E^{\circ} = \frac{E_{pc} + E_{pa}}{2} \quad (1.3)$$

The number of electrons transferred in the electrode reaction (n) for a reversible couple can be determined from the separation between the peak potentials.

$$\Delta E_p = E_{pa} - E_{pc} \cong \frac{0.059}{n} \quad (1.4)$$

Slow electron transfer at the electrode surface, "irreversibility", causes the peak separation to increase. The peak current for a reversible system is described by the Randles-Seveik equation shown in equation 1.5. for the forward sweep of the first cycle.

$$I_p=(2.69\times10^5)n^{3/2}AD^{1/2}Cv^{1/2} \tag{1.5}$$

where I_p is peak current (A), n is electron stoichiometry, A is electrode area (cm^2), D is diffusion coefficient (cm^2/s), C is concentration of substance (mol/cm^3) and v is scan rate (V/s).

Accordingly, peak current increases with square root of scan rate and is directly proportional to concentration. The relationship to concentration and scan rate is particularly important in analytical applications and in studies of electrode mechanisms.

The electrochemical analysis system consists of 3 important parts as follows : the recording system, The potentiostat and the electrochemical cell. In this research, an application on a smartphone was developed as software for recording, display and storage the electrochemical signal. This application communicates with potentiostat by using Bluetooth protocol. Potentiostat was used as a device for controlling voltage and detecting current from an electrochemical reaction. The electrochemical cell part consists of an electrode and a redox couple. There are 3 electrodes in cyclic voltammetic technique as follows: a working electrode (WE), a counter electrode (CE) and, a reference electrode (RE). A redox couple consists of electrolyte and sample. The testing setup is shown in the figure 1.3.

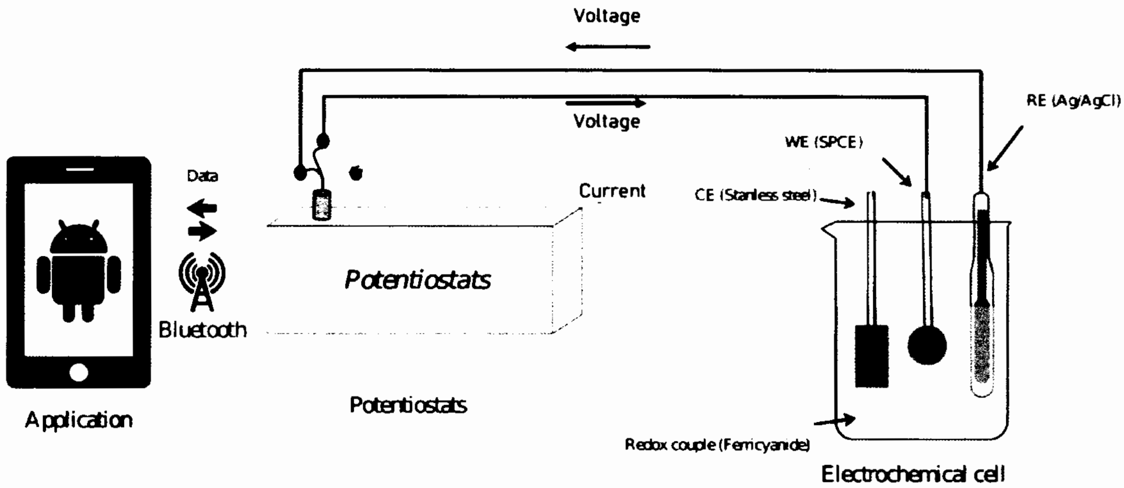

Figure 1.3 Equipment setup for an electrochemical analysis system testing

1.2 Related research

Voltammetry is a kind of electrochemical analysis that the result comes from the relation between a current generated by a chemical reaction. This technique is important for the study about an elementary process of redox reaction in various state, the reverse ability of sample in a redox reaction, the electron stoichiometry of a system, the diffusion coefficient of a substance , and the formal reduction potential. Polarography is the first technique in a group of voltammetric analysis. This technique was invented by Jaroslav Heyrovsky, the Czechoslovak Republic chemist, in 1922 caused him to win the Nobel Prize in 1959 [6]. Heyrovsky measured the result of current occurred from chemical reaction after stimulated by electric power. The mercury drop electrode was used as a working electrode in his experiment. The results were analyzed by using the relationship between the current from a reaction and the stimulation voltage. The results indicated that there is a lot of current flow through the working electrode at some stimulation voltage which varies in each substance. After the studies more, he concludes that the current has come from a chemical reaction between a sample substance and electrode. This invention is very useful in analytical chemistry and it was called that Polarography. The plot between the stimulation voltage and current is called polarogram. After that, there are several techniques in voltammetry group that were studied and developed. However, the education is quite inconvenient, because the equipment is not as modern as it should be. In 1942, Archie Hickling developed the automatic voltage controller called a potentiostat [7]. This device was used for three electrode systems which was an advancement for the field of electrochemistry. However, the device still has many restrictions that need to be continuing to develop. After the prototype of Archie Hickling, researcher interested continuously in the development of potentiostat. In 2014, Andres Felipe Diaz Cruz et al. developed the low-cost and miniaturized potentiostat to generate signal for cyclic voltammetry which is one of technique in voltammetric analysis [8]. They used this device as a portable healthcare monitoring device. The LMP91000EVM [9] was used as main potentiostat module which was controlled by Beaglebone microcontroller. The result indicated efficiency and sensitivity of developed potentiostat is quite great. Moreover, the developed potentiostat is more compact and lower price compared with commercial device. The analytical data was saved into SD card. Likewise, in 2015, the development to improve the efficiency of the general potentiostat was studied by Karlheinz Kellner, et al. [10]. This research used the LP097 as a potentiostat module, the ATMEGA328 as a main controller unit and the POTCON as a software for user interface, display and storage. The result shown the good stability and ability to manage noise. The 16-bit, signal converter was used, so the potentiostat have more resolution and accuracy in signal detection. Moreover, the developed device has a wide current detection range. The experimental data was sent to computer in real time. The data was analyzed, displayed and saved in a computer by using the POTCON software. In 2016, N. A. Nordin, et al. design and implement a readout circuit that can capture redox reaction of an electrolyte and sense small current changes in working electrode of 3-electrode electrochemical biosensor measurement system by using operation amplifier (OP-AMP), a standard amplifier device, low-cost and compact [11]. The developed circuit consist of several circuit as follow: Difference amplifier, Voltage follower amplifier, Voltage adder amplifier and Current to voltage converter. The testing result found the percentage error of peak current measurement is 7.69% while the percentage error of voltage at the point the current peak is 3.63% compared with the standard lab potentiostat. In 2017, Sarika Bukkawar et al. developed the portable potentiostat for using in Linear sweep voltammetry [12]. The aim of this research is to develop the high efficiency, high resolution and low-cost potentiostat. The ATMEGA328 was used as main microcontroller. The ADS1220, 24-bits analog to digital converter and the

DAC8574, 16-bits digital to analog converter were used as the converter unit for output signal and input signal, respectively. The results indicated the resolution of input voltage at 769 nA and the minimum current detected by device was 125 nA. the experimental information was stored in form of text file (.txt) on computer.

Based on the research previously mentioned, all have to use computer to process and store data. In the last few years, a smartphone is an electronic device that has been developed to be a good processing ability and storage equivalent to a computer. Advantage of smartphone compared to computer is size that smaller and it can communicate by using wireless network. Therefore, researcher interested in the development of devices used in scientific work by using a smartphone as devices to process and store data instead of computer. In 2016, Diming Zhang and Qingjun Liu developed biological measuring equipment by using various sensor on the smartphone [13]. For the example, they used a camera to construct Microscopic bio-imaging, Fluorescence biosensors and Colorimetric biosensors. In addition, they also developed the electrochemical measuring device by using the smartphone as a data analysis device, data collection and display device. The developed equipment can be used with many techniques such as Amperometry, Potentiometry and Impedimentary. In 2017, Daizong Ji, et al. developed the potentiostat for using in cyclic voltammetry by using the smartphone as a display, storage and processing device [14]. Glucose detection was used in device testing. The result indicated that the device has high efficiency and stability when compared to standard equipment that is more expensive. When testing by using Glucose sample in the human blood cell, found that the minimum concentration of glucose that can be detected is 0.026 mM. The percent error compared to the standard device is 4% .

1.3 The aim of research

In this research, potentiostat for using in 3-electrode cyclic voltammetry and the recording system based on application on smartphone will be designed and fabricated. The developed device must be the more compact size and low-cost. The working of recording system together with potentiostat will be tested and demonstrated for the performance of developed device such as the stability, the sensitivity and the accuracy

The scope of study includes:

(1) The low-cost miniaturized potentiostat for using in 3-electrode cyclic voltammetry will be designed and developed.

(2) An application on Android smartphone will be developed for using as a recording system.

(3) The working of recording system together with potentiostat will be tested by using the screen-printed carbon electrode (SPCE) as a working electrode, A silver chloride electrode (Ag/AgCl) as a reference electrode, Stainless steel as a counter electrode and potassium ferricyanide/ferrocyanide as a redox couple.

The developed system is useful for research and development in electrochemical field in the future.

CHAPTER 2
POTENTIOSTAT CONSTRUCTION AND DEVELOPMENT OF RECORDING SYSTEM

2.1 Potentiostat construction

2.1.1 Principle of potentiostat

In this work, potentiostat is used to provide the voltage control between two electrodes, working and reference electrodes as a constant value, in chemical and biological analysis. Besides the voltage control, measurement of the current occurred from chemical reaction is another function of the potentiostat [15]. In general electrochemical analysis, the system is typically operated in a three electrode cell which include abovementioned working and reference electrodes as well as a counter electrode as shown in figure 2.1. The reference electrode's role is to act as a reference in measuring and controlling the working electrode potential, without passing any current. The reference electrode should have a constant electrochemical potential at low current density. The most common reference electrodes are the saturated calomel electrode and the Ag/AgCl electrode. The working electrode is the electrode in an electrochemical system on which the reaction of interest is occurring. Common working electrodes can consist of materials ranging from inert metals such as gold, silver or platinum, to inert carbon such as glassy carbon, boron doped diamond or pyrolytic carbon, and mercury drop and film electrodes. Chemically modified electrodes are employed for the analysis of both organic and inorganic samples. The counter electrode, often also called the auxiliary electrode, is an electrode used in a three-electrode electrochemical cell for voltammetric analysis or other reactions in which an electric current is expected to flow. Auxiliary electrode is often fabricated from electrochemically inert materials such as gold, platinum, or carbon [16].

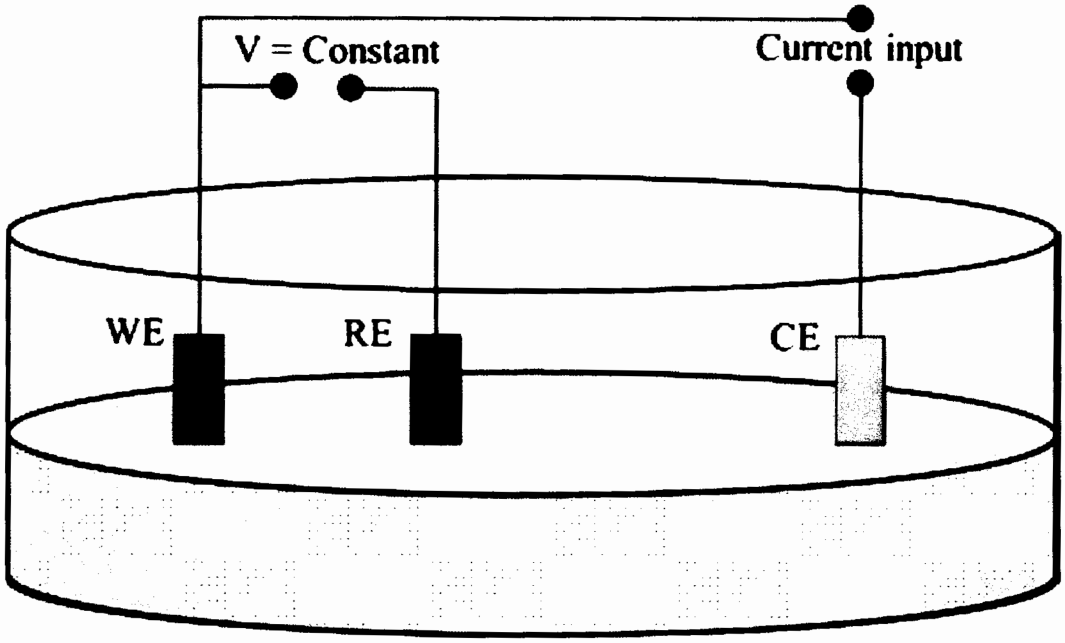

Figure 2.1 The three-electrode electrochemical system

The potentiostat component consists of signal generator, signal detector, control amplifier and current detector as shown in Figure 2.2.

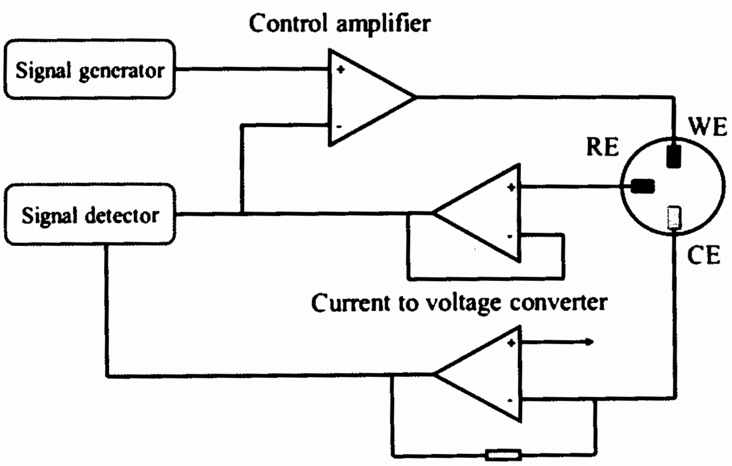

Figure 2.2 A schematic representation of a three electrode potentiostat

The signal generator creates the signal form requested from the user (e.g., constant value, ramp, sine wave) and sends it to the control amplifier. Before the signal was applied to the electrochemical cell, the voltage will be optimized by the control amplifier. The optimization is signal fusion between signal from signal generator and feedback signal from a reference electrode. The potential difference between reference and working electrodes is measured at the signal detector. The current flow through the cell is measured at the current detector. In this section, the current signal is converted to a voltage signal. The voltage affected from current flow is detected by a signal detector.

2.1.2 Design and fabrication of potentiostat

2.1.2.1 Signal generator

The signal generator is a part of electronic device that using for generating the stimulus voltage for electrochemical cell. The signal generator is controlled by microcontroller. Because of microcontroller is a digital device, it cannot directly produce the stimulus signal for electrochemical cell which is an analog. Therefore, the MCP4822 device is used to transform digital signal to analog signal.

The MCP4822 is dual 12-bit digital to analog converter. The device operates from a single 2.7 V to 5.5 V supply with serial peripheral interface (SPI) and have a high precision internal voltage reference (V_{REF} = 2.048 V). The full-scale range of the device can be configured to be 2.048 V or 4.096 V by setting the gain selection option bit (gain of 1 of 2). The user can select DAC (DAC_A or DAC_B) channel by the configuration channel selection bit [17]. The devices provide high accuracy and low noise performance for consumer and industrial applications where calibration or compensation of signals (such as temperature, pressure and humidity) are required.

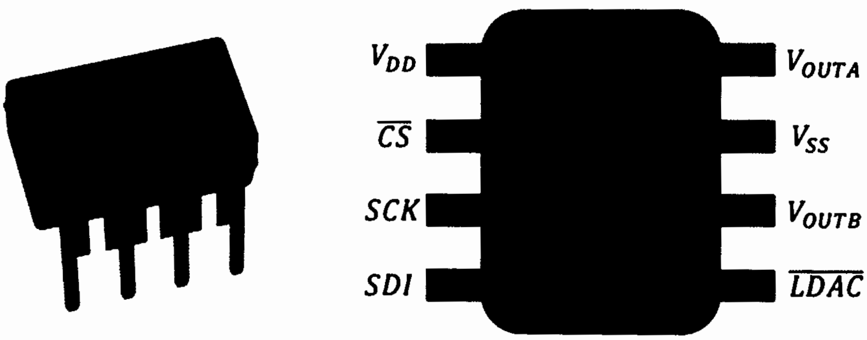

Figure 2.3 The MCP4822 package type (8-pin PDIP) and pinout [17]

Table 2.1 Pin function table for MCP4822 [17]

MCP4802/MCP4812/MCP4822 MSOP/PDIP/SOIC	Symbol	Description
1	V_{DD}	Supply voltage input (2.7 V to 5.5 V)
2	$\overline{CS}$	Chip select input
3	SCK	Serial clock input
4	SDI	Serial Data input
5	$\overline{LDAC}$	Synchronization input
6	V_{OUTB}	DAC_B output
7	V_{SS}	Ground reference
8	V_{OUTA}	DAC_A output

The MCP4822 is available in the 8-pin PDIP package as shown in Figure 2.3 The descriptions of pins are listed in Table 2.1.

Supply voltage input pin (V_{DD}) is the positive input voltage ranged from 2.7 V to 5 V related to Ground reference (V_{SS}). The power supply should be clear voltage as much as possible for a good DAC performance. The guide is suggested to use an appropriate bypass capacitor of about 0.1 μF (ceramic) to ground. An additional 10 μF capacitor (tantalum) in parallel is also recommended to further attenuate high frequency noise presented in an application board [17].

Ground reference point (V_{SS}) is the pin of analog ground reference point. This pin must be faced with the ground plane by using a low impedance connection.

Chip select input (CS), Serial clock input (SCK) and Serial data input (SDI) are the serial peripheral interface pin which are the chip select input pin, which requires an active low to enable serial clock and data functions, the SPI compatible serial clock input pin and the SPI compatible serial data input pin, respectively.

Latch DAC synchronization input pin is the pin that used for transferring DAC setting to their corresponding DAC output register. Both of DAC output channel will be updated when this pin is low logic. If user require DAC output updating at the rising edge of CS pin, user can joint this pin to ground (V_{SS}).

Analog output pin (DAC_A and DAC_B) is the analog output pin A and B. Each output has its own output amplifier. The full-scale range is determined by the gain selection option (1x or 2x). The DAC analog output cannot go higher than the supply voltage (V_{DD}).

As the mentioned above, the MCP4822 12-bit digital to analog converter has the serial peripheral interface (SPI) as a communication protocol. The SPI is a type of short distance communication between devices. The devices that communicated by using SPI were called master and slave. The master device is used to handle all the communication. All of configuration in SPI communication such as the format of data and frequency of serial clock were determined by master. In general, the SPI has 4 wire of signal which are SCK, MOSI, MISO and CS. The SCK wire is used to send serial clock from master to slave. The data from master is transmitted through MOSI wire to slave device. In contract, the data from slave is sent to master by using MISO wire. In case of more than one slave device, CS wire is used to enable communication between the master and the required slave [18].

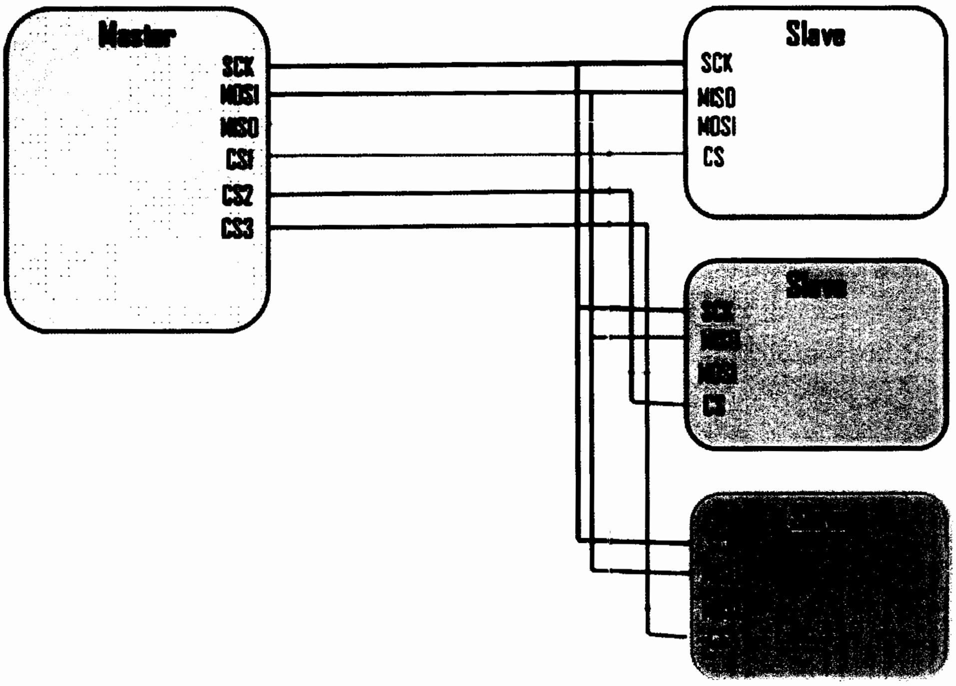

Figure 2.4 Serial peripheral interface (SPI) working diagram

The MCP4822 is designed to directly interface with SPI port in mode 0,0 and mode 1,1, available on many microcontrollers. Commands and data are sent to the device via the SDI pin, with data being clocked-in on the rising edge of SCK. The CS pin must be held low for the duration of a write command. The write command consists of 16 bits and is used to configure the DAC's control and data latches. Table 2.2 shows the write command for each device.

Table 2.2 Write command register for MCP4822 (12-bit DAC) [17]

W-x	W-x	W-x	W-0	W-x	W-x	W-x	W-x	W-x	W-x	W-x	W-x	W-x	W-x	W-x	W-x
$\overline{A}$/B	-	$\overline{GA}$	$\overline{SHDN}$	D11	D10	D9	D8	D7	D6	D5	D4	D3	D2	D1	D0
bit 15															bit 0

Each of write command bit is used to configure the working of the MCP4822 which consist of channel selection, gain selection and shutdown mode control.

Bit 15 or $\overline{A}$/B bit is a channel selection bit. DAC_A will be available when bit 15 is active low. In contract, if user want to active DAC_B , bit 15 need to be high logic.

Bit 14 is don't care bit. This bit can be high or low logic. Its haven't affect about the configuration of the MCP4822.

Bit 13 or $\overline{GA}$ bit is the output gain selection bit. If logic was set to be high, gain of DAC is 1x. if $\overline{GA}$ bit has low logic, gain is 2x.

Bit 12 or $\overline{SHDN}$ bit is used to control shutdown mode. Shutdown mode of MCP4822 is useful for saving energy. Logic high of this bit is spend for active mode operation, analog output is available. If this bit is low, shutdown mode will be enabled, the selected channel is shutdown, Analog output is not available at the channel that was shut down.

Bit 11-0 is DAC input data bit.

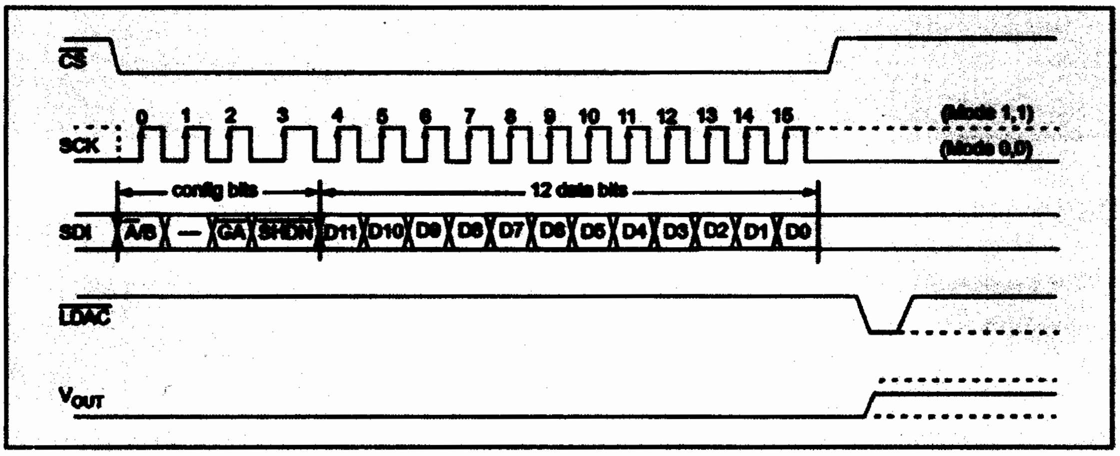

Figure 2.5 Write command timing diagram [17]

The write command is initiated by driving the $\overline{CS}$ pin low, followed by clocking the four configuration bits and the 12 data bits into the SDI pin on the rising edge of SCK. The $\overline{CS}$ pin is then raised, causing the data to be latched into the selected DAC's input registers. The MCP4822 devices utilize a double buffered latch structure to allow both DAC_A's and DAC_B's outputs to be synchronized with the $\overline{LDAC}$ pin, if desired. By bringing down the $\overline{LDAC}$ pin to a low state, the contents stored in the DAC's input registers are transferred into the DAC's output registers (V_{OUT}), and both V_{OUTA} and V_{OUTB} are updated at the same time. All writes to the MCP4822 devices are 16-bit words. Any clocks after the first 16th clock will be ignored. The most significant four bits are configuration bits. The remaining 12 bits are data bits. No data can be transferred into the device with $\overline{CS}$ high. The data transfer will only occur if 16 clocks have been transferred into the device. If the rising edge of $\overline{CS}$ occurs prior, shifting of data into the input registers will be aborted. The DAC input coding of this devices is straight binary. The analog output voltage is shown in equation 2.1

$$V_{OUT} = \frac{2.048\ V \times D_n}{2^n} \times G \qquad (2.1)$$

Where 2.048 is the internal voltage reference, D_n is digital input code, G is gain selection (1x and 2x) and n is DAC resolution which is 12-bit for MCP4822.

For an operation of signal generator, a very simple circuit as shown in Figure 2.6 was fabricated to generate the stimulus voltage for electrochemical cell. The voltage level was control by a microcontroller. The output voltage is followed equation 2.1.

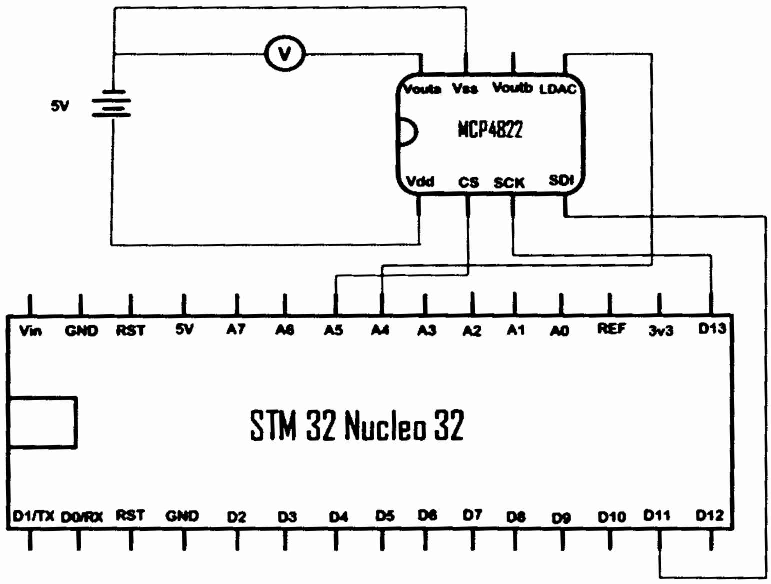

Figure 2.6 The schematic design of the signal generator

In Figure 2.6, the microcontroller is a main device that used to control voltage level and get command from user. The command from user have a 16-bit format which consist of 4-bit configuration and 12-bit data. The maximum of output voltage is 2.048 V, 0.5 mV of resolution for 1x of gain selection and 4.096 V, 1 mV of resolution for 2x of gain selection. The range of 12-bit data is from 0 to 4096.

The control program flowchart is indicated in figure 2.7. The code was generated and put into the microcontroller. The input data was sent through the communication protocol from computer or smartphone to microcontroller. The data was transformed into digital code for continuously sent to the MCP4822. The output voltage19 will change according to input digital code and its was measured by a voltmeter.

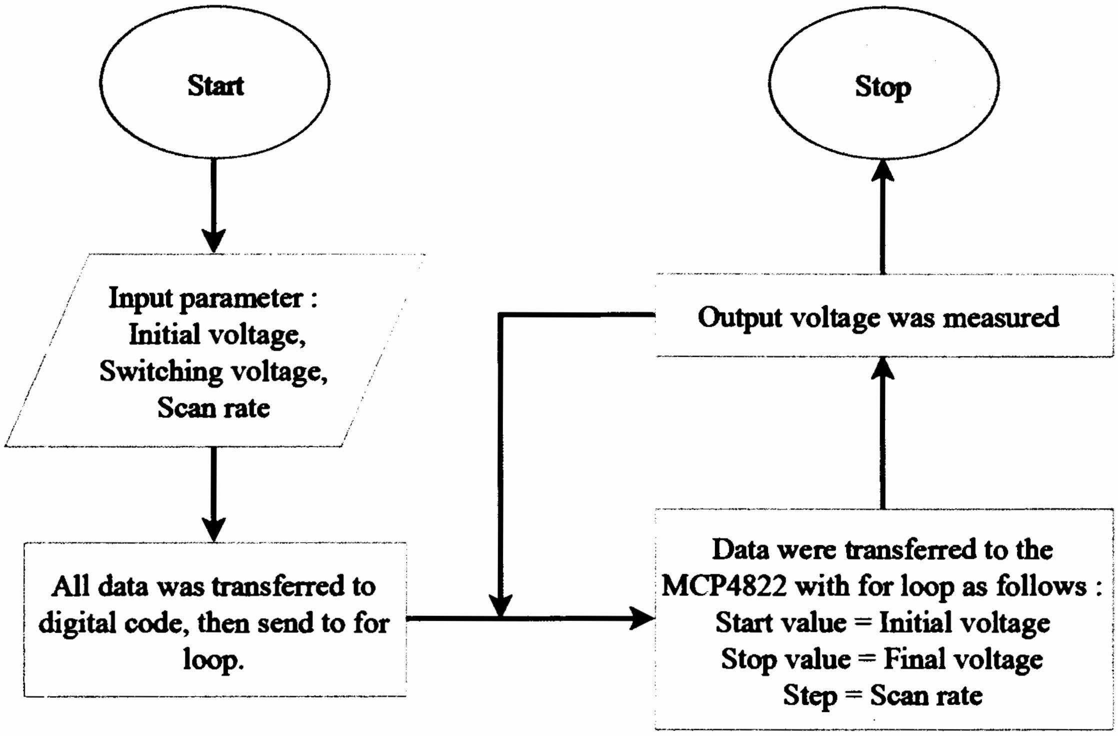

Figure 2.7 The flowchart for signal generator program

The signal generator will be tested at various conditions, i.e. the gain selection, the voltage range and exchange rate of voltage. Figure 2.8 shows the analog output for signal generator testing in 1x gain selection. The result shows good linearity signal at 10 Hz of frequency, 0 to 4095 of digital input range and 50 mV/s of exchange rate. Moreover, it shows a maximum voltage which is about 2.00 V at 4096 digital input.

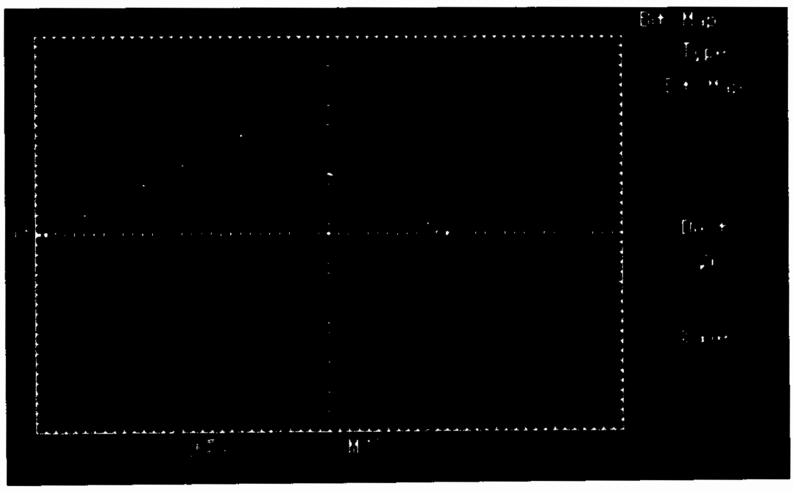

Figure 2.8 The analog output for signal generator at 1x gain selection

The 2x gain selection testing was indicated in figure 2.9. All of parameters were defined as the previous experiment. The results show the maximum output voltage which is about 4.00 V at 4096 of digital input.

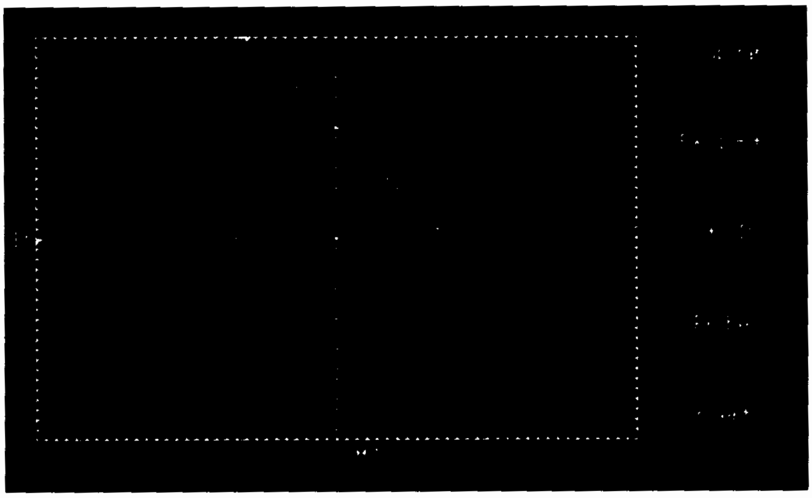

Figure 2.9 The analog output for signal generator at 2x gain selection

2.1.2.2 Signal detector

In electrochemical analysis, after the electrochemical cell is activated then the electrochemical reaction occurs, there will be an electric current flow through an electrode. The relation of peak current and the stimulus voltage can point out the properties of electrode and sample substance. In this project, the signal detector has 2 functions. Firstly, the signal detector was used to detect input signal which is the stimulus signal for electrochemical cell. Secondly, it was used for the measuring of current that occurred from electrochemical reaction. The main control unit of signal detector is microcontroller which is responsible for controlling the operation of the signal detector and receiving the information obtained from the measurement to be sent to the display device. In term of the working characterization of the signal detector, because of the output signal which is current from an electrochemical reaction is an analog signal, but the microcontroller cannot directly receive an analog signal, therefore, the signal must be transformed to a digital signal. For that reason, the MCP3202 which is 12-bit analog to digital converter is used in this work.

The MCP3202 is a successive approximation 12-bit analog-to-digital (A/D) converter which can be programed to provide a single pseudo differential input pair or dual single-ended inputs. The communication of this device is done by using a simple serial peripheral interface (SPI). The conversion rate of the MCP3202 is capable at 100 ksps and 50 ksps at 5.0 V and 2.7 V of supply voltage, respectively. Low-current design permits operation with typical standby and active currents of only 500 nA and 375 μA for 2.7 V and 5V power supply, respectively. The MCP3202 that used in this work is offered in 8-pin PDIP packages [19] as shown in Figure 2.10.

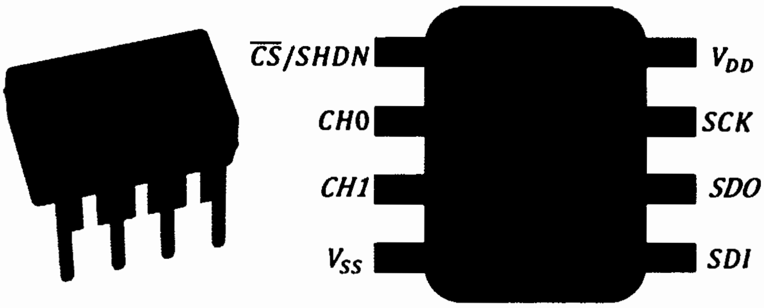

Figure 2.10 The MCP3202 packages type (8-type PDIP) and pinout

Table 2.3 Pin function table for the MCP3202 [19]

MCP3202 MSOP/PDIP/SOIC	Symbol	Description
1	$\overline{CS}$/SHDN	Chip select and shutdown input
2	CH0	Channel 0 analog input
3	CH1	Channel 1 analog input
4	V_{SS}	Ground reference
5	SDI	Serial Data input
6	SDO	Serial Data output
7	SCK	Serial clock
8	V_{DD}/V_{REF}	2.7 V to 5.5 V Rower supply and Reference voltage input

The $\overline{CS}$/SHDN pin is used to initiate communication with the device when pulled low and will end a conversion and put the device in low power standby when pulled high. The $\overline{CS}$/SHDN pin must be pulled high between conversions.

The CH0 and CH1 pin are an analog input channel 0 and channel 1, respectively. These channels can be programmed to be used as two independent channels in single ended-mode or as a single pseudo-differential input where one channel is positive input (IN+) and one channel is negative input (IN-). The information in Table 2.4 is shown the programming of the channel configuration.

Table 2.4 The channel and mode configuration bit for MCP3202 [19]

	Config Bits		**Channel Selection**		**GND**
	Sgl/Diff	**Odd/Sign**	**CH0**	**CH1**	
Single Ended Mode	1	0	+	Shutdown	-
	1	1	Shutdown	+	-
Pseudo-differential Mode	0	0	IN+	IN-	
	0	1	IN-	IN+	

The information in Table 2.4 shows the configuration choice of using the analog input channels configured as two single-ended inputs or a single pseudodifferential input. Configuration is done as part of the serial command before each conversion begins. If the single ended mode is required to used channel 0 as an input channel, the config bit must be 1 and 0 for Sgl/Diff and Odd/sign, respectively. In contrast, if user want to used channel 1 as an input channel, both of config bits must be 1. When used in the pseudo-differential mode, CH0 and CH1 are programmed as the IN+ and IN- inputs as part of the command string transmitted to the device. The IN+ input can range from IN- to V_{REF} (V_{DD} + IN-). The IN- input is limited to ±100 mV from the V_{SS}.

The SCK pin is a serial clock pin for the serial peripheral interface. This pin is used to initiate a conversion and to clock out each bit of the conversion as it takes place.

The SDI and SDO pin are a serial data input and output pin. The SDI was used to clock in input channel configuration data. The SDO was used to shift out the results of the A/D conversion.

Figure 2.11 shows the function block diagram of the MCP3202 12-bit analog to digital converter. The operation of MCP3202 is as follows : The input channel was selected by the input channel mux according to configuration bit from the control logic. the input signal was sent to the sample and hold. The signal on the sample and hold part will be sent to convert to the digital data by the 12-bit SAR digital-to-analog converter along with the clock signal. After data was converted, it will be transferred to shift register and sent out to a serial output pin.

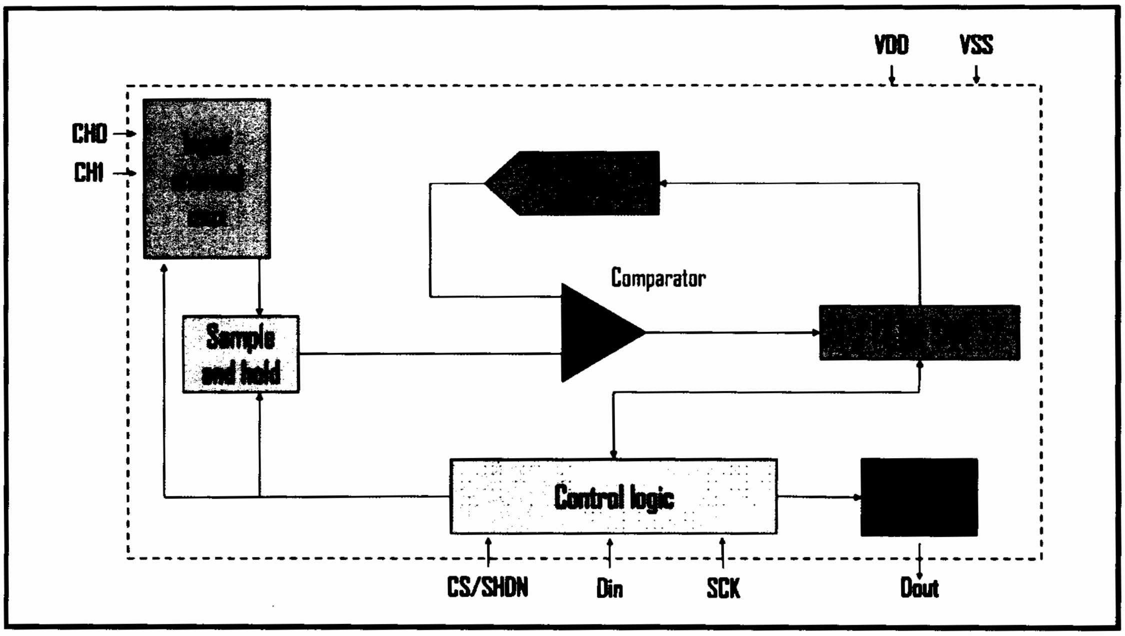

Figure 2.11 The function block diagram of the MCP3202 [19]

The digital output code produced by an A/D Converter is a function of the input signal and the reference voltage. For the MCP3202, VDD is used as the reference voltage. As the VDD level is reduced, the LSB size is reduced accordingly. The theoretical digital output code produced by the A/D Converter is shown below.

$$D_{OUT} = \frac{4096 \times V_{in}}{V_{DD}} \tag{2.2}$$

Where D_{OUT} is a digital output code, Vin is an analog input voltage and V_{DD} is a supply voltage.

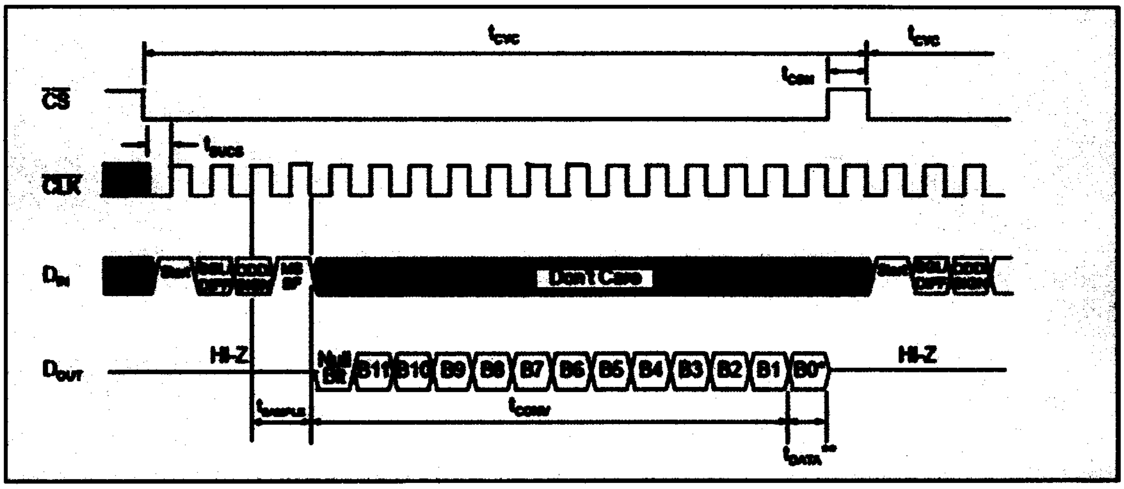

Figure 2.12 Communication with the MCP3202 using MSB first format only [19]

Communication with the MCP3202 is done by using a standard SPI compatible serial interface. The initiation is started by the activation of $\overline{CS}$ line with low logic. If the device was powered up with the $\overline{CS}$pin low, it must be brought high and back low to initiate communication. When the $\overline{CS}$ pin low and the SDI pin high, the first clock that was received will constitute a start bit. The SGL/DIFF bit and the ODD/ SIGN bit follow the start bit and are used to select the input channel configuration as shown in Table 2.2. Moreover, another function of the SGL/DIFF bit is the selections of single ended or pseudo-differential mode. Also, The ODD/SIGN bit is used to select which channel is used in single ended mode and is used to determine polarity in pseudodifferential mode. The bit that follows the ODD/SIGN is the MSBF bit. The MSBF bit is transmitted to enable the LSB first format or the MSB first format. If the MSBF bit is high, then the data will come from the device in MSB first format and any further clocks with $\overline{CS}$ low will cause the device to output zeros. If the MSBF bit is low, then the device will output the converted word LSB first after the word has been transmitted in the MSB first format. In the data process, the input data format was divided into 3 bytes. The first byte is contained only start bit which will be transferred add the first rising edge of the clock. The output byte after start bit was received is just only zero. The device will start to sample the analog input on the second rising edge of the clock, after the start bit has been received. The second byte is contained by 3 config bit and 5 don't care bit. The output byte is consisting of the first three bit as zeros, one bit of null and the 4 bits of MSB data as a last four bit. lastly, the LSB data will be sent back after the last byte input was received. The MSB data and LSB data will be combined to be 12-bit digital data. If all 12 data bits have been transmitted and the device continues to receive clocks while the $\overline{CS}$ is held low, the device will output the conversion result LSB first as shown in Figure 2.13 If more clocks are provided to the device while $\overline{CS}$ is still low, the device will clock out zeros indefinitely.

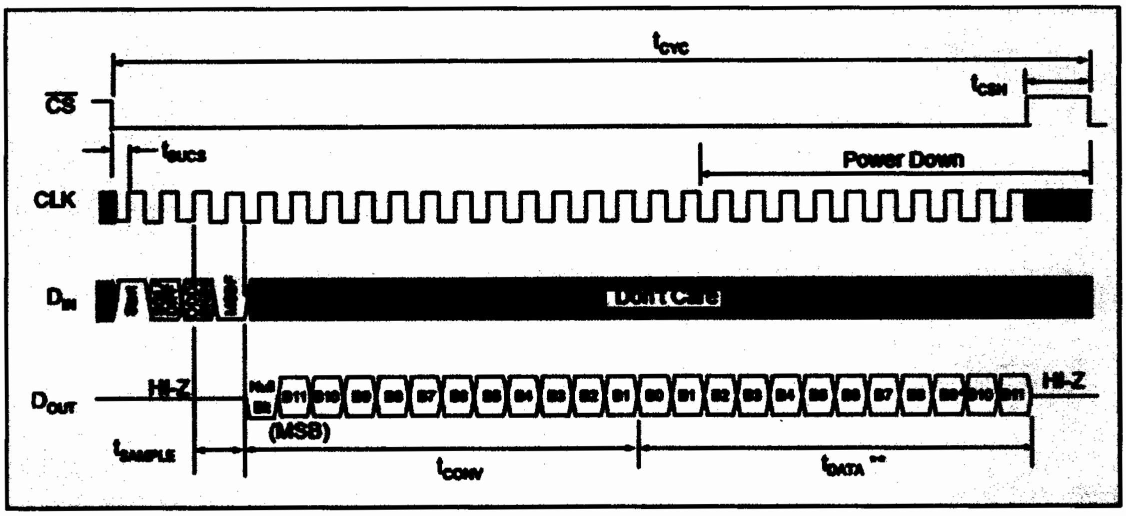

Figure 2.13 Communication with the MCP3202 using LSB first format only [19]

For an operation of signal detector, a simple circuit for the MCP3202 was performed to detect a voltage signal by using both input channel as shown in Figure 2.14. The process, configuration and analytical data were controlled by a microcontroller.

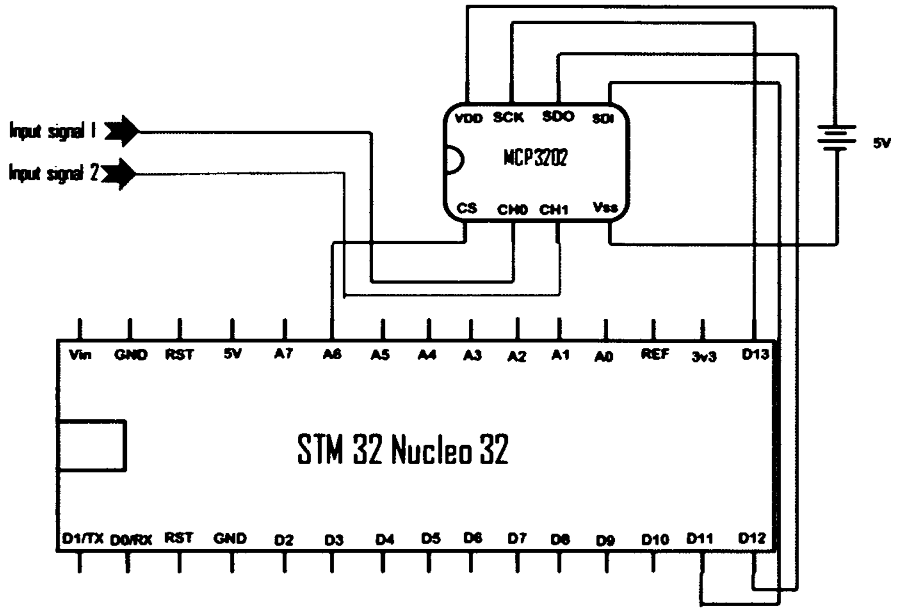

Figure 2.14 The schematic design of the signal detector

The STM 32 Nucleo32 microcontroller was used as a main control unit. It was used to generate a configuration bit and clock signal for the MCP3202.The config bit was sent from microcontroller to the MCP3202 via SDI line along the pulse of clock signal in SCK line. Moreover, the data that is the feedback from the converting signal of the MCP3202 will be get by microcontroller through the SDO line then analyzed and continuously sent to a display device.

The flowchart displayed in Figure 2.15 demonstrates the working steps of program. The working was started by the forcing of the CS line to low logic. Then, the first byte which is in binary format and act as a start command bit will be sent to MCP3202. The output after sent this byte is just only null byte. At the rising edge of the next clock, the second byte which contains the configuration bit will be transferred. The configurations were determined as follows : the working mode that was selected is single ended mode, the CH0 was used as an input channel and the MSB first format was chosen to be the output data format. The output from this step is the 4-MSB bits which is converted from analog signal from the CH0. Then, the third byte which is don't care will be continuously transferred to the MCP3202. The feedback data of this step is the 8-LSB bits. The MSB and LSB will be combined to be 12-bit output data and analyzed by microcontroller. Continuously, the CS line will be forced to be high logic to finish a communication. After that, the program will be run again by the same process, but the CH1 will be set as the input channel. lastly, the output data will be sent to the display device. From the sampling rate of the MCP3202 which is 100 ksps at 5 V of supply voltage, it indicates that the device can run at high frequency. Therefore, it seems that the input signal at both channels can be detected at the same time.

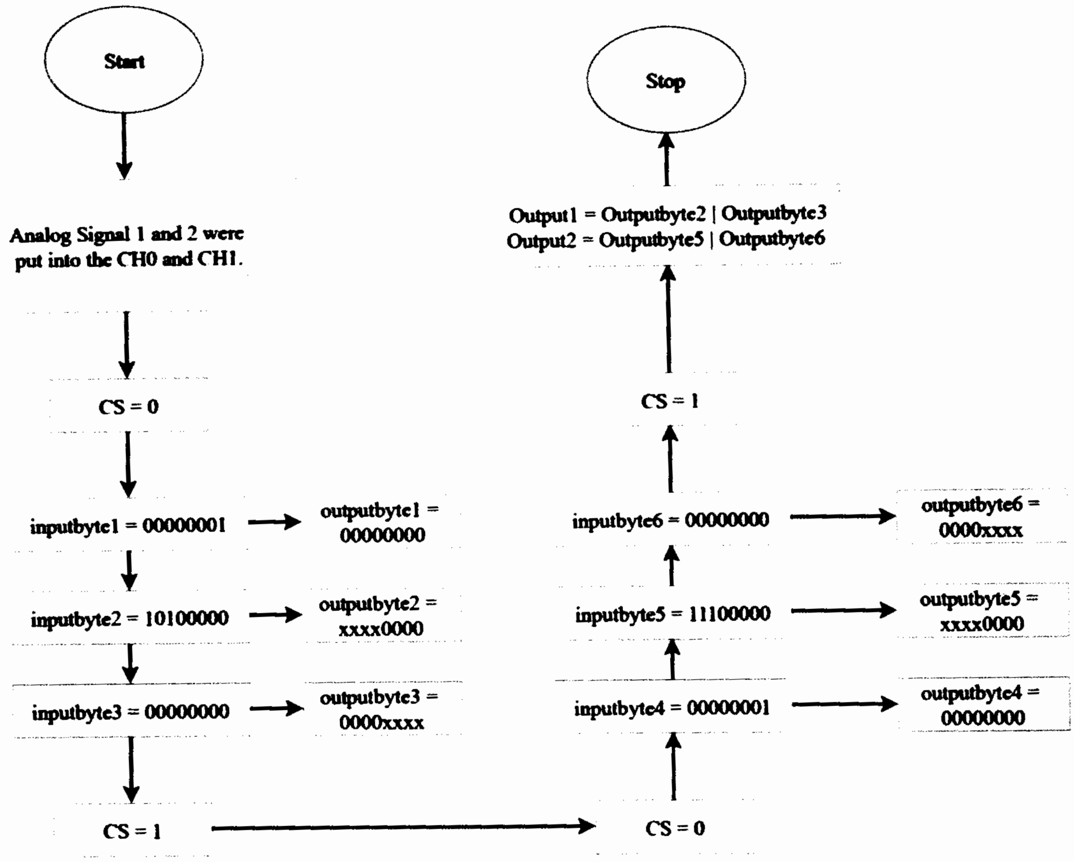

Figure 2.15 The flowchart for the signal detector program

2.1.2.3 Control amplifier

As we know well, the signal generator that was developed in this project can apply the voltage signal in range of 0 to 4 V. The voltage that released from the signal generator is just only positive voltage. However, many techniques of electrochemical analysis, including voltammetry require both positive and negative voltages. Moreover, the stimulus voltage of an electrochemical cell must be the differential voltage between the working electrode and the reference electrode. Therefore, the voltage must be optimized before applying to an electrode. In this work, the control amplifier was developed to use in voltage optimization. The main device that used to fabricate the control amplifier is an operation amplifier (OP-AMP). The operation amplifier will be used to construct various amplifier circuit.

The differential amplifier circuit is one of the amplifier circuit that used for control amplifier fabrication. This circuit was used to transform the range of voltage from 0 to 4 V to -2 to 2 V. Figure 2.16 shows the circuit design of a differential amplifier circuit.

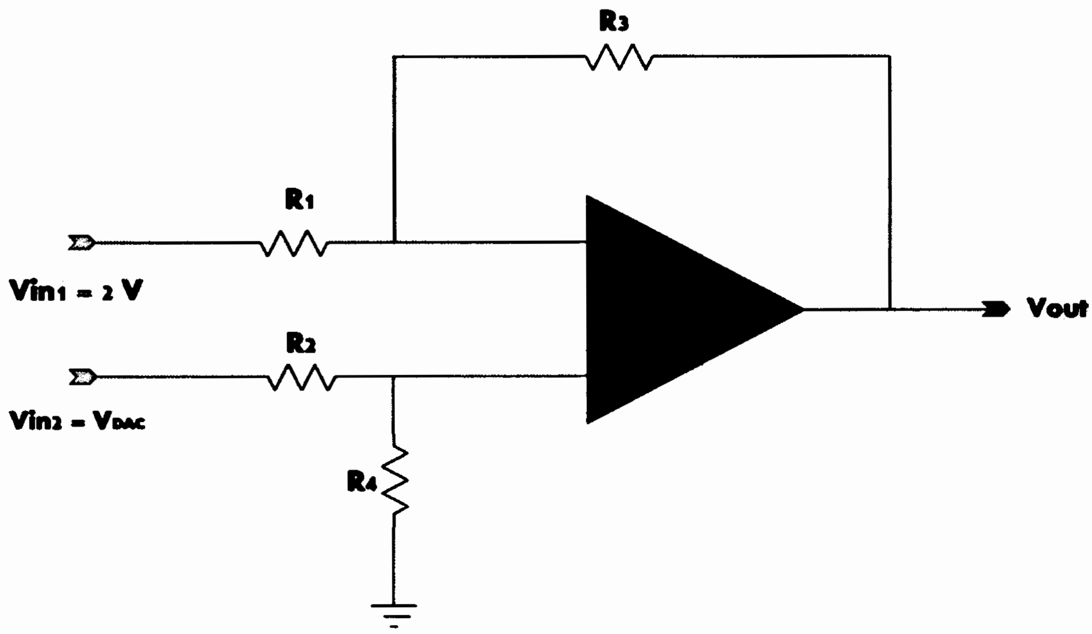

Figure 2.16 The circuit design of differential amplifier

The differential amplifier circuit is used to amplify the difference between two voltages making this type of operational amplifier circuit a subtractor [20]. By connecting each input in turn to ground, the superposition can be used to solve for the output voltage. The equation 2.3 shows an output voltage of a differential amplifier circuit.

$$V_{out} = -V_{in1}\left(\frac{R_3}{R_1}\right) + V_{in2}\left(\frac{R_4}{R_2+R_4}\right)\left(\frac{R_1+R_3}{R_1}\right) \tag{2.3}$$

If all the resistors are all the same ohmic value, then the circuit will become a unity gain differential amplifier and the voltage gain of the amplifier will be exactly one or unity. Then the output expression would simply be as follows equation 2.4

$$V_{out} = V_{in2} - V_{in1} \quad (2.4)$$

In this work, all of resistor were set to have same value, so the differential amplifier circuit become a unity gain amplifier circuit. Therefore, the output voltage will become

$$V_{out} = V_{DAC} - 2V \quad (2.5)$$

Where V_{DAC} is the output voltage from the signal generator.

The testing results of differential amplifier circuit were shown in Figure 2.17 The result demonstrated that the input signal was transformed from the signal in the range of 0 to 4 V (Blue line) to the signal in the range of -2 to 2 V (Yellow line).

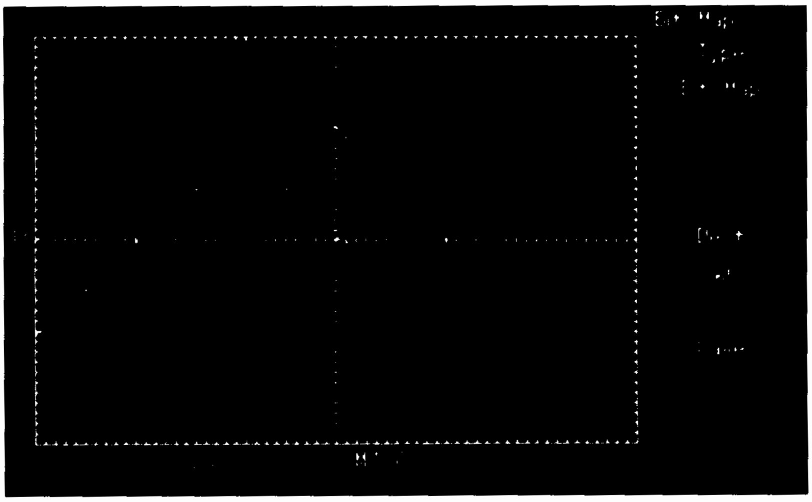

Figure 2.17 The testing results of differential amplifier circuit

After the input signal from the signal generator was transformed by the differential amplifier, it cannot be directly applied to electrochemical cell. The signal must be managed for one more step because the stimulus signal for electrochemical cell must be the differential voltage between working electrode and reference electrode. For this reason, it is necessary to develop another part of control amplifier circuit.

The first circuit that used is the voltage follower (sometimes called voltage buffer). The voltage follower was used to receive feedback voltage from the reference electrode. The function of voltage follower circuit is a protection from the effect of current or loading the previous stage unacceptably and interfering with its desired operation [21]. Because of a voltage follower generally has a high input impedance and a low output impedance, so whatever circuit is supplying the input signal does not have to provide much current, while the output of the voltage follower can supply significantly more current to the next stage.

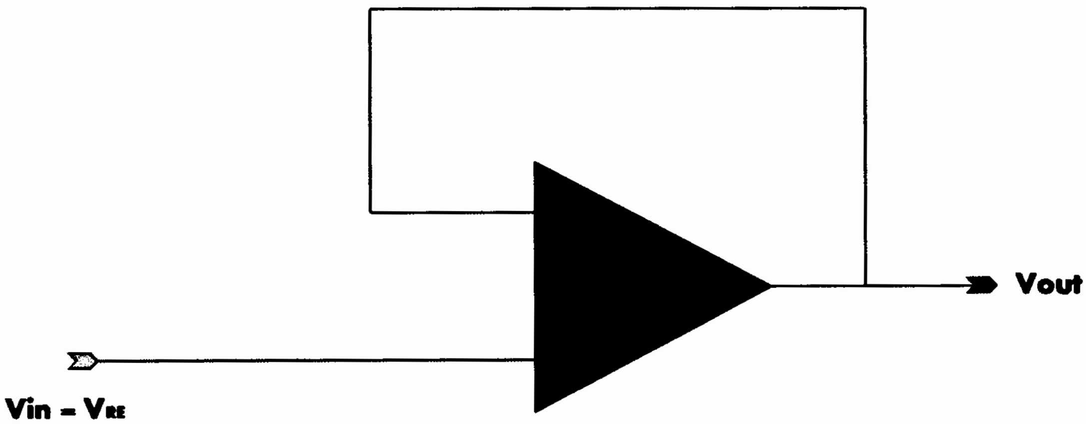

Figure 2.18 The circuit design of voltage follower

The voltage follower can be simply constructed by using op-amp as shown in Figure 2.18. The wiring of this circuit is just connecting the output of the op-amp to its inverting input and connecting the signal source to the non-inverting input. The voltage gain of this circuit is one. The entire output voltage is fed back into the inverting input. The difference between the non-inverting input voltage and the inverting input voltage is amplified by the op-amp. This connection forces the op-amp to adjust its output voltage simply equal to the input voltage as shown in equation 2.6

$$V_{out} = V_{in} \tag{2.6}$$

The testing results of the voltage follower is shown in Figure 2.19. The result indicates that the output voltage (Yellow line) is equal to input voltage (Blue line). The output signal from voltage follower was continuously transferred to next stage for performing the stimulus signal.

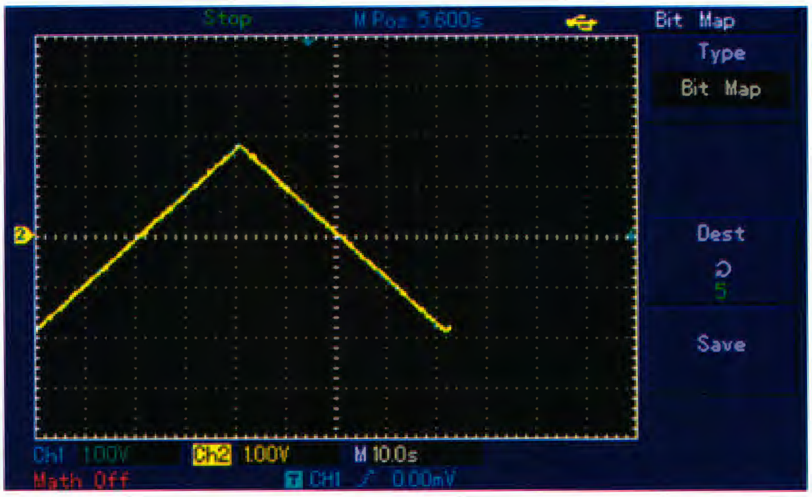

Figure 2.19 The testing results of the voltage follower

As mentioned above, the stimulus signal is a differential voltage between working electrode and reference electrode. Therefore, the stimulus voltage will be performed by using the signals from differential amplifier and voltage follower.

The circuit that used for the management is the summing amplifier. A summing amplifier is an op-amp based circuit where multiple input signals of different voltages are added [22]. For this reason, summing amplifier is also called as voltage adder since its output is the addition of voltages present at its input terminals. There are 2 types of a summing amplifier which are inverting summing amplifier and non-inverting summing amplifier. The summing amplifier uses an inverting amplifier configuration, i.e., the input is applied to the inverting input terminal of the op-amp, while the noninverting input terminal is connected to ground. From this configuration, the output of voltage adder is out of phase with respect to the input signal by 180 degree. However, the stimulus signal must be the in-phase signal with the input signal, so the circuit that was used in this section is the non-inverting summing amplifier. A non-inverting summing amplifier can also be constructed by using the non-inverting amplifier configuration. For this type, the input voltages are applied to the non-inverting input terminal and a part of the output is fed back to the inverting input terminal, through voltage-divider-bias feedback. A non-inverting summing circuit that was design for using in this work which is shown in the Figure 2.20.

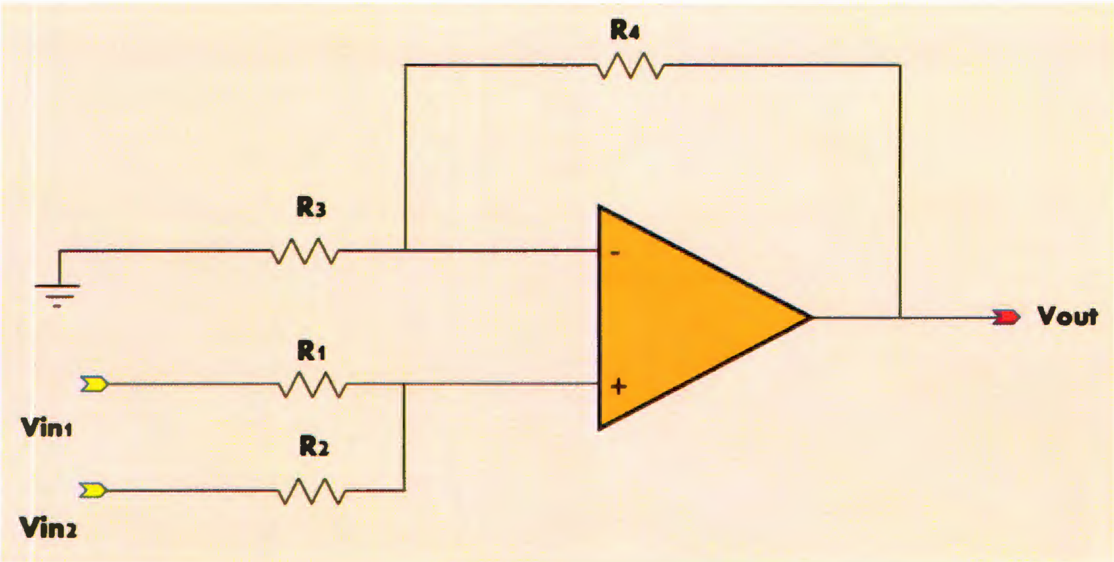

Figure 2.20 The circuit design of non-inverting summing amplifier

For a non-inverting summing amplifier with two input, its output voltage will be as follows:

$$V_{out} = \left(1 + \frac{R_4}{R_3}\right)\left(\left(V_{in1} \times \frac{R_2}{R_1 + R_2}\right) + \left(V_{in2} \times \frac{R_1}{R_1 + R_2}\right)\right) \qquad (2.7)$$

In this work, the researcher just only wants to add the feedback voltage from the reference electrode to the signal from the signal generator without amplifying the signal. For adding the input voltages without amplifying, the value of input resistance(R_1 and R_2) must be chosen equal to that of the feedback resistor (R_3 and R_4). Therefore, the output voltage will be as follows:

$$V_{out} = V_{in1} + V_{in2} \tag{2.8}$$

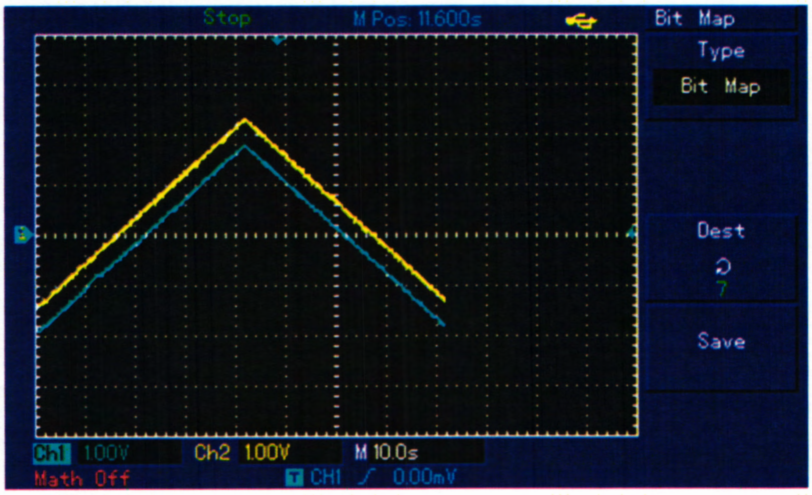

Figure 2.21 The output signal from the non-inverting summing amplifier

The non-inverting summing amplifier was tested by inputting the signal from signal generator optimized by the differential circuit and the feedback voltage from the reference electrode. when assume that the voltage from reference electrode is 500 mV, the result shown in Figure 2.21 indicates that the output signal has an increase of 500 mV compared to the input signal. Moreover, the output signal is based on the equation 2.8.

Before the signal will be provided to electrochemical cell, the signal will be handled again with a voltage follower circuit to ensure that the stimulus signal has the effect from current as low as possible. The assembly between the non-inverting summing amplifier and the voltage follower was shown in Figure 2.22.

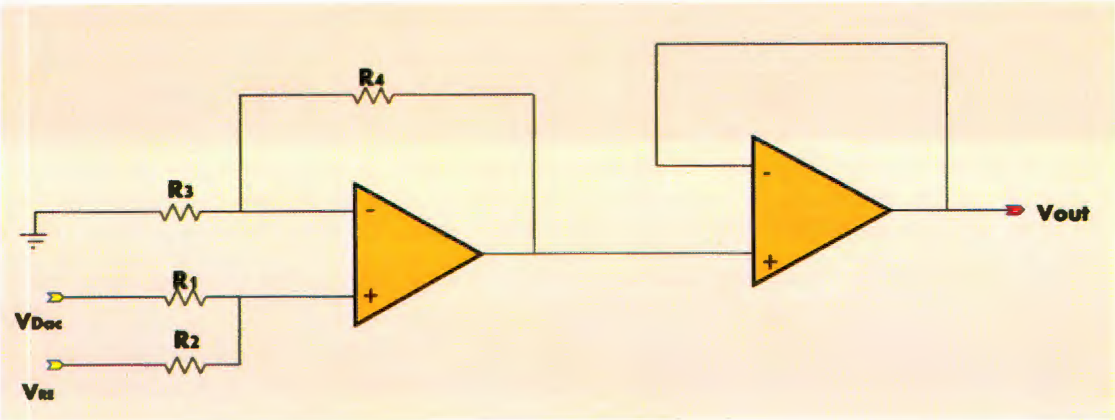

Figure 2.22 The assembly between the non-inverting summing amplifier and the voltage follower

From the various circuits mentioned above, which consist of the differential amplifier, the voltage follower and the non-inverting summing amplifier were combined to construct the control amplifier. The circuit diagram of control amplifier was shown in Figure 2.23.

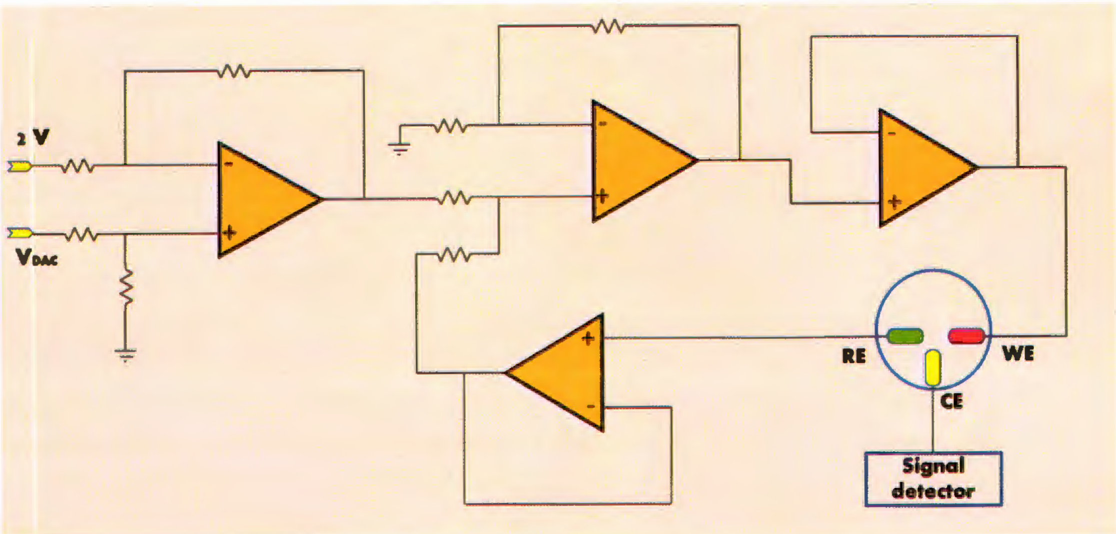

Figure 2.23 The circuit diagram of control amplifier

The control amplifier circuit was tested by providing voltage in the range of -2 to 2 volts from a signal generator circuit. To measure the input voltage, the measuring is based on the voltage difference between working and reference electrode.

The results shown in Figure 2.24 indicate that the output signal is equal to the input signal.

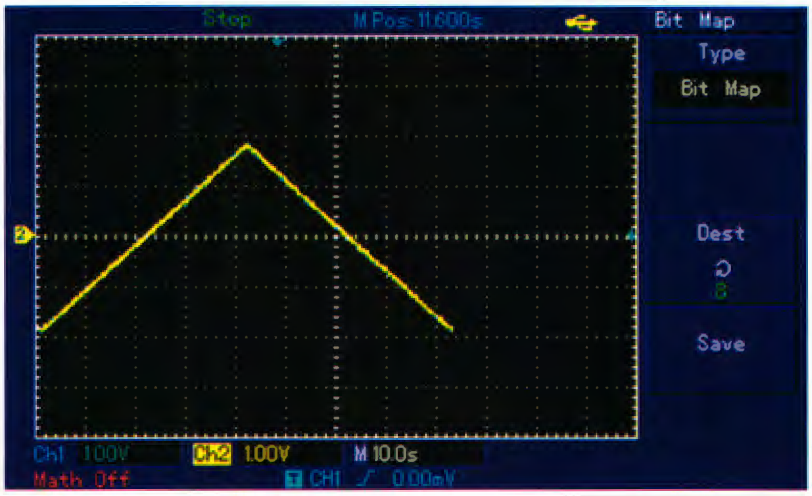

Figure 2.24 The circuit diagram of control amplifier

2.1.2.4 Current detector

As we know well, after the electrochemical cell was excited, the reaction will occur then the current will flow between the working electrode and counter electrode. The current from the reaction will indicate both quantitative and qualitative property of electrode and chemical substance. Because of the detection device can not directly measure the current, so the current must be converted to voltage. If your instrument has an input impedance that is several orders larger than the converting resistor, a simple resistor circuit can be used to do the conversion. However, if the input impedance of the instrument is low compared to the converting resistor then the following op-amp circuit should be used. The circuit that was used to convert the current to voltage is shown in Figure 2.25.

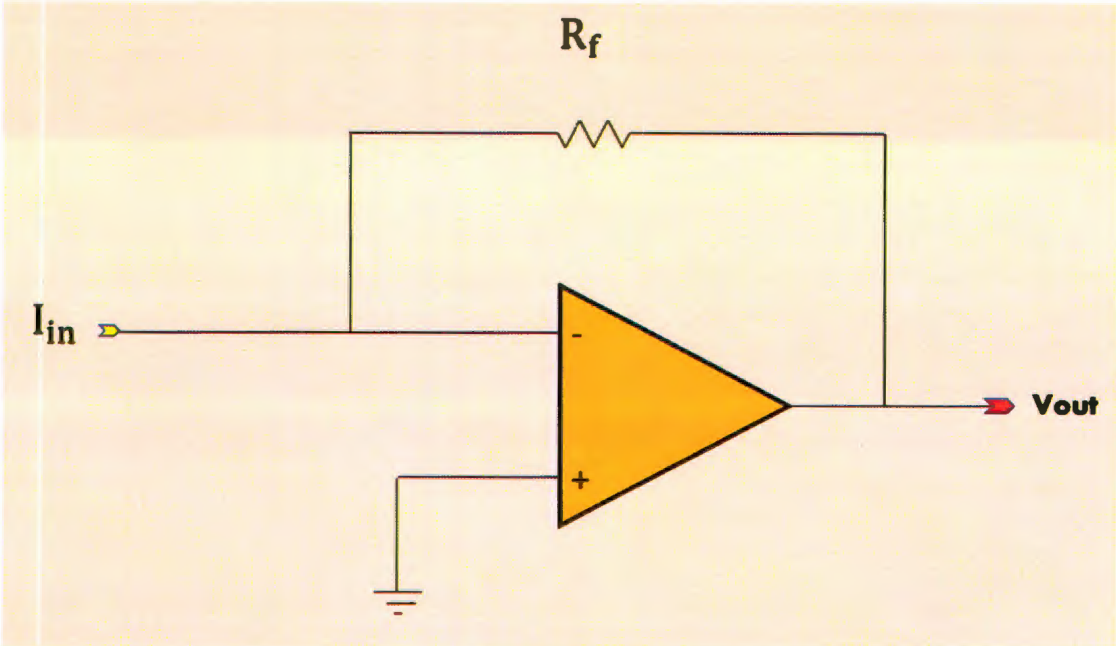

Figure 2.25 The circuit diagram of the current to voltage converter

A current to voltage converter will produce a voltage proportional to the given current [23]. This circuit is required if the measuring instrument is capable only of measuring voltages and we need to measure the current output.

To analyze the current to voltage converter by inspection, if we apply the input current to node at the inverting input (V^-) and let the input current to the inverting input be I^-, then

$$\frac{V^- - V_{out}}{R_f} = I_{in} + I^- \tag{2.9}$$

since the output is connected to V− through Rf, the op-amp is in a negative feedback configuration. Thus

$$V^- = V^+ = 0 \tag{2.10}$$

Where V^+ is a voltage at the non-inverting input. For ideal op-amp, the input current to the inverting input (I^-) is equal 0. Therefore

$$V_{out} = -I_{in}R_f \tag{2.11}$$

Equation 2.11 indicates that the output voltage varies along with the input current. If the input current is positive, the output voltage will be negative. In contrast, the output voltage will be positive when the input current is negative.

Because of the signal detector can only measure positive signals, but the output signal of current to voltage converter can be both positive and negative, so it is necessary to construct a circuit for signal optimization.

The optimization for this part is to make the output signal of the current to voltage converter become a positive signal even if the input current is negative or positive. The circuit that was used for optimization is the inverting summing amplifier as shown in Figure 2.26.

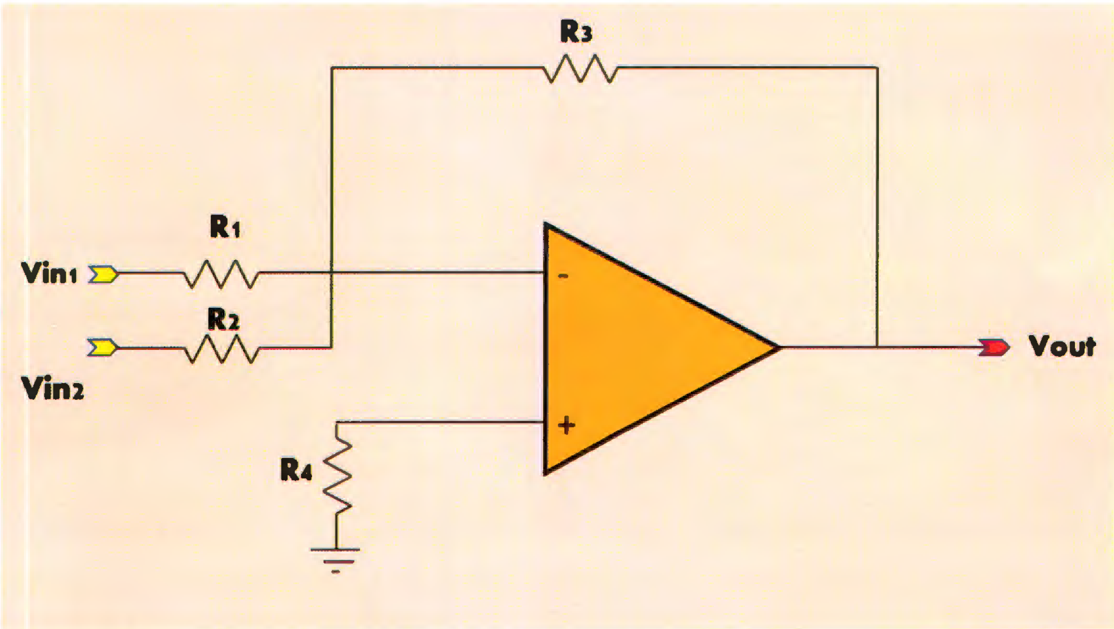

Figure 2.26 The inverting summing amplifier circuit

The inverting summing amplifier is a voltage adder like the noninverting summing amplifier that the input signal is the summation of signal at the input terminal of op-amp, but the difference is the input signal of this circuit is on the inverting pin and non-inverting is wired to ground. the output of this circuit will be out of phase with respect to the input signal by 180 degree [22]. The output voltage of this circuit is based on the equation 2.12.

$$V_{out} = -\left(\left(\frac{R_3}{R_1} \times V_1\right) + \left(\frac{R_3}{R_2} \times V_2\right)\right) \tag{2.12}$$

However, the gain of this circuit must be equal to 1 because the researcher only wants to use this circuit as a circuit for combining input signals. To let the gain of the circuit equal to 1, all the resistor must be equal. Thus, the output will be as follows:

$$V_{out} = -\left(V_{in1} + V_{in2}\right) \tag{2.13}$$

From equation 2.13, If we provide Vin1 equal to the output voltage of the current to voltage converter and Vin2 equal to -2.5 V, then

$$V_{out} = \left(I_{in} R_f + 2.5V\right) \tag{2.14}$$

Due to the signal detector can measure the signal in the range of 0 to 5 V, so from equation 2.14 indicates that the maximum output voltage of the current to voltage converter is equal to 2.5 V and -2.5 V for positive voltage and negative voltage, respectively. Therefore, it means that the range of current that the device can measure will depend on the feedback resistor of current to voltage converter circuit (R_f).

After the signal was optimized by the inverting summing amplifier, the signal will be filtered by low-pass filter circuit as shown in Figure 2.27.

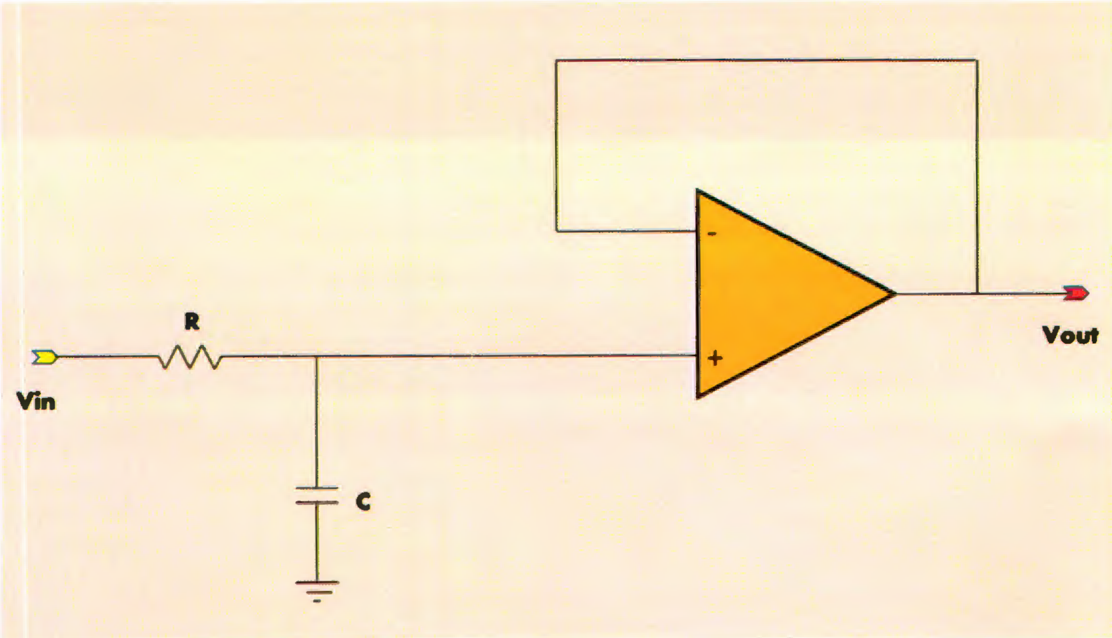

Figure 2.27 The circuit diagram of the low-pass filter

The low-pass filter is a circuit that passes signals with a frequency lower than a selected frequency (sometime called cutoff frequency) and attenuates signals with a frequency higher than the cutoff frequency. The cutoff frequency depends on the filter design.

The low-pass filter sometime called RC low-pass filter is similar to the voltage divider circuit. Thus, it can be determined by using the following equation:

$$V_{out} = V_{in} \times \left(\frac{R_2}{R_1 + R_2} \right) \quad (2.15.)$$

Where R1+R2 = RT , the total resistance of circuit.

When the signal was applied to low-pass filter circuit, the reactance of a capacitor (Xc) varies inversely with frequency, while the value of the resistor remains constant as the frequency changes. At low frequencies, the capacitive reactance of the capacitor will be very large compared to the resistive value of the resistor. This means that the voltage potential across the capacitor will be much larger than the voltage drops across the resistor. we also know that the capacitive reactance of a capacitor is given as

$$X_c = \frac{1}{2\pi fC} \tag{2.16}$$

Where f is frequency and C is capacitor value.

For a series circuit consisting of a single resistor in series with a single capacitor, the circuit impedance (Z) is calculated as:

$$Z = \sqrt{R^2 + X_c^2} \tag{2.17}$$

Thus, by using the potential divider equation of two resistors in series and substituting for impedance we can calculate the output voltage of an RC Filter for any given frequency as follows:

$$V_{out} = V_{in} \times \left(\frac{X_c}{\sqrt{R^2 + X_c^2}} \right) \tag{2.18}$$

The various circuits mentioned in this part were combined to construct a current detector circuit. The current to voltage converter was used to transform the current from electrochemical reaction to voltage. The inverting summing amplifier was used for signal optimization to make the suitable signal for signal detector. Lastly, the low-pass filter was used to filter the frequency unsuitable signals. The combination of these circuit is shown in Figure 2.28.

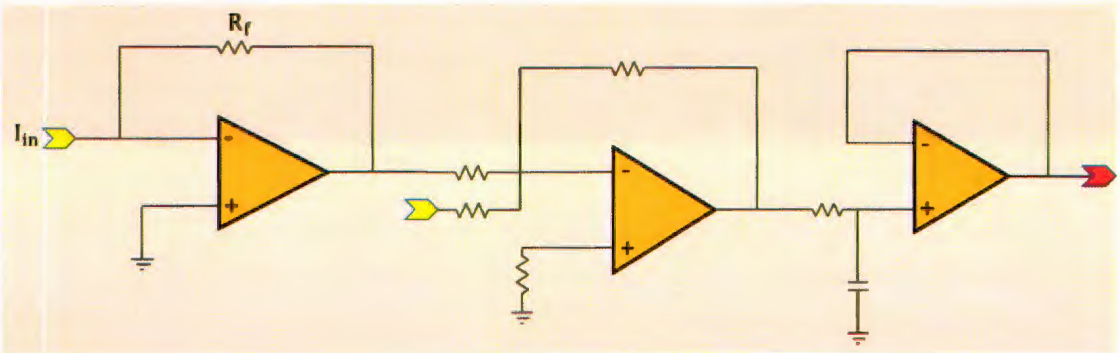

Figure 2.28 The combination circuit of current detector

The current detector circuit was tested by applying a current into circuit, then the voltage signals were detected by using the signal detector (MCP3202). The voltage results were calculated to know the input current by using theoretical prediction. The predicted results were compared with the results measured by the Agilent Digital Multimeter. The compared results shown in Figure 2.29 indicated the good performance in current signal measurement of the developed circuit.

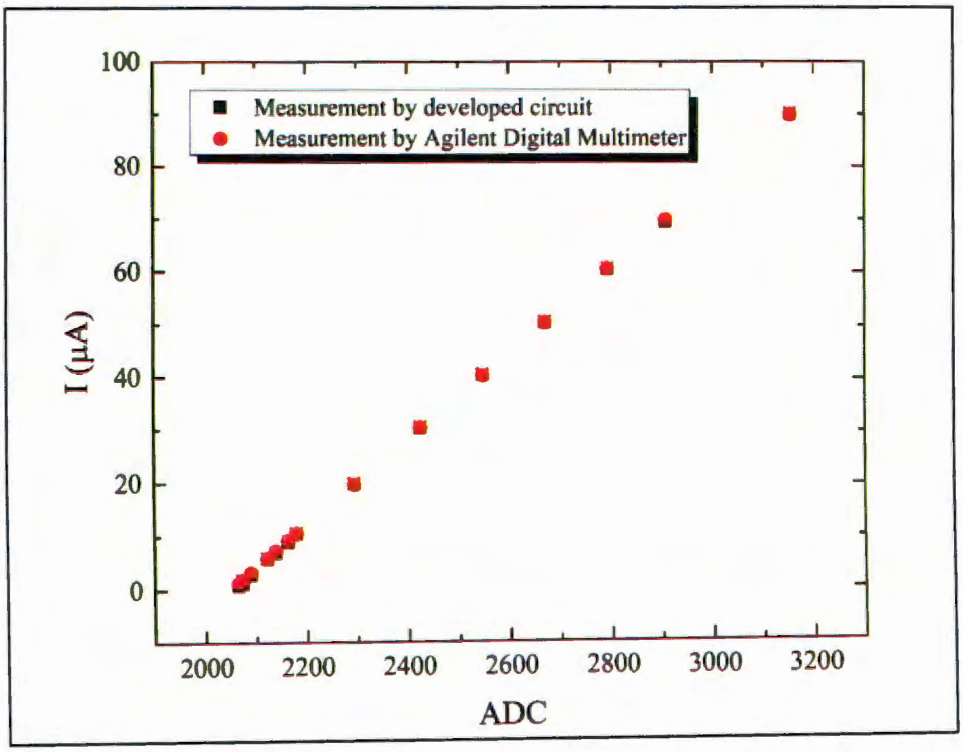

Figure 2.29 The testing results compared between the developed circuit and an Agilent Digital Multimeter

2.2 Recording system development

2.2.1 The general detail of recording system

In this research, the recording system was developed for using in 2 functions. Firstly, it was used to determine the working of the potentiostat for cyclic voltammetry operation. As we know well about the analytical method of electrochemical with cyclic voltammetry, the researcher must define various parameters which consist of the pretreatment voltage, the initial voltage, the switching voltage, the number of scan and scan rate to be appropriate for the experiment. The second function of the recording system is to use as a display and storage device. The system will display and save data in real time. User can export the data file to analyze and make a report.

For the general system, computer was used as a recording device. In this research, we wanted to develop a different recording equipment. The goal of development is to develop a system that is more compact, portable and cheaper than the commercial system.

A smartphone is a device that can do more than other phones. it works as a computer but are mobile devices small enough to fit in a user's hand. Because smartphones are small computers, they run an operating system that is often common between devices to ensure compatibility. Most can do multitasking, running more than one program which helps the user do things quicker and easier. Smart phones can send and receive data much faster than older phones and close to the computer. There are many ways to send and receive data with other device, such as internet, Bluetooth and USB port, etc. Users can get more programs, called mobile apps, from the manufacturer's app store which can help them complete special tasks [24].

In addition to the application in an app store, user can design and develop an application by themselves. There are many platforms that can be used to develop an application. However, the platform that was used in this work is the online platform called MIT App Inventor.

MIT App Inventor is an intuitive, visual programming environment that allows everyone to build fully functional apps for smartphones. Methods of application development of this platform is blocks-based tool. This method facilitates the creation of complex, high-impact apps in significantly less time than traditional programming. The MIT App Inventor project seeks to democratize software development by empowering all people, especially young people, to move from technology consumer to technology creator. MIT App Inventor is a cloud-based tool, which means users can build apps right in their web browser. The users can learn how to build their own apps and start to do it by visiting at ai2.appinventor.mit.edu [25].

2.2.2 Design and fabrication

An application that was developed in this work consists of the following parts: connection management, parameter input part, display part and data file.

The connection management was used for communication control between recording system and potentiostat. In this work, both devices communicate with Bluetooth signals.

The parameter input part was used to receive all of parameter as mentioned above from user to send to potentiostat.

The display part was consisting of 2 parts which is data display and graph display. The displayed graph is only preliminary. User can analyze data by using data in a data file.

The operation of the system will follow the flow chart shown in Figure 2.30. The application was shown in Figure 2.31.

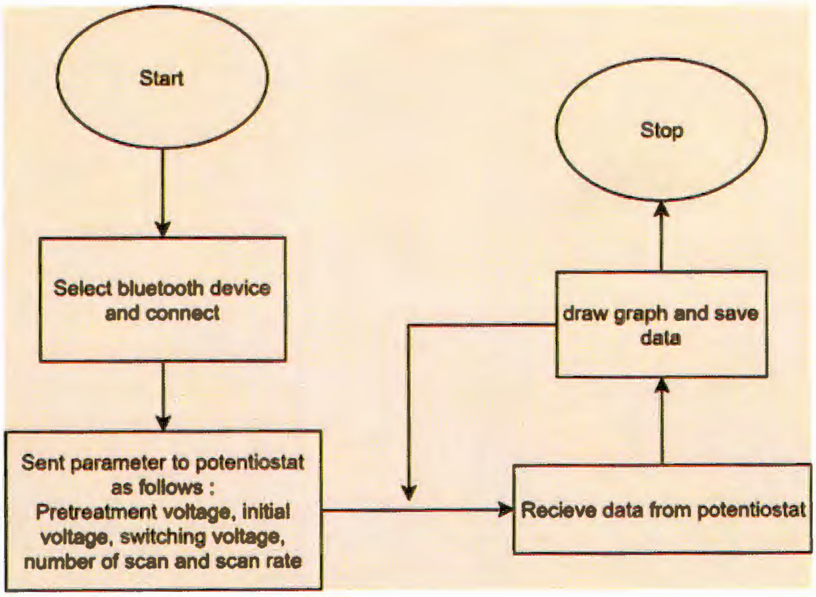

Figure 2.30 Flowchart diagram of the recording system

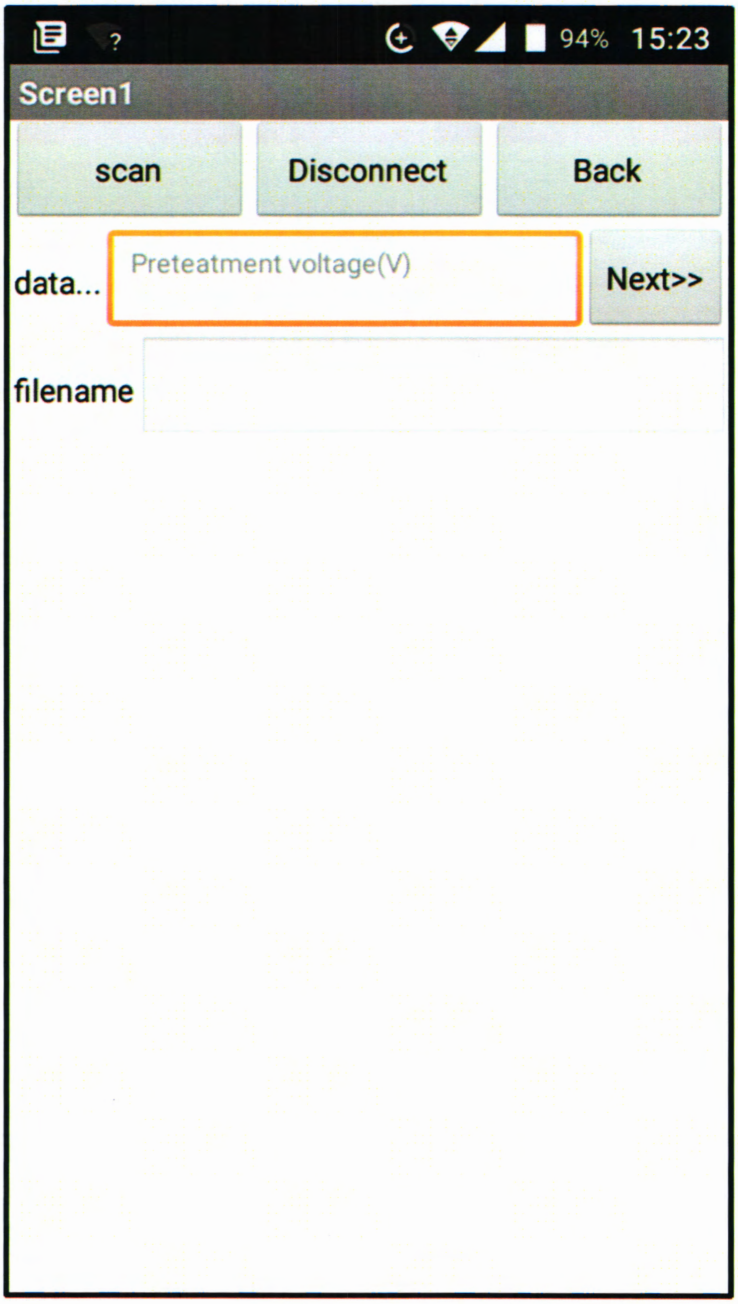

Figure 2.31 The initial screen of the recording application

The initial screen will show various components. The "Scan" button was used to find nearby Bluetooth devices. The "Disconnect" button was used to disconnect with potentiostat after completing the experiment. The input textbox was used to fill in the various parameters. The "Next" button was used to press for sending data to potentiostat. Free space below was used to display the plotting of data received from potentiostat.

The step of using the application is as follows. Firstly, user must press the scan button. After pressing the button, a Bluetooth device will appear as shown in Figure 2.32.

Figure 2.32 The list of Bluetooth device scanned by application

User must select the Bluetooth device that belong to the potentiostat. In this work, the BT04-A module was used as a communication equipment between the potentiostat and a smartphone. After selected, this screen will disappear, then a new window as shown in Figure 2.32 will appear.

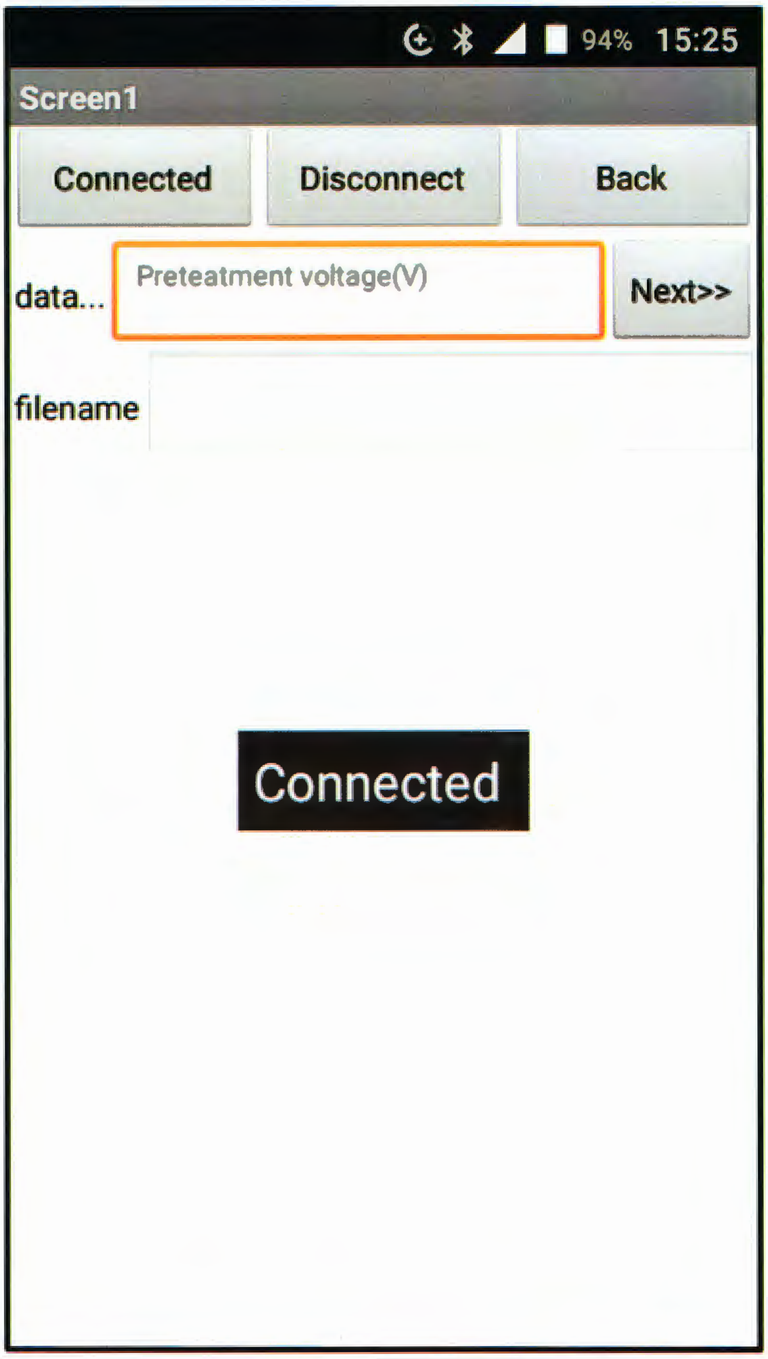

Figure 2.33 The screen after the Bluetooth was connected

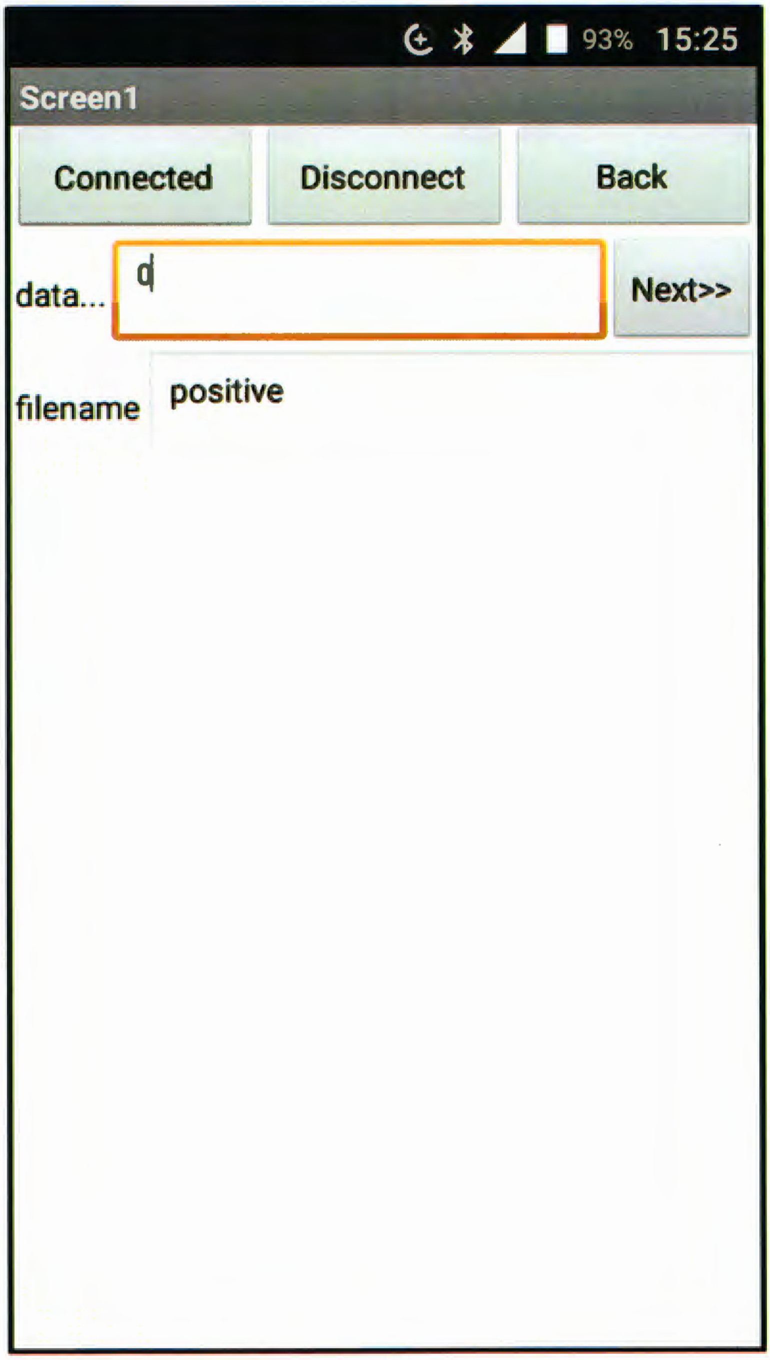

Figure 2.34 The screen after filling a filename for saving data

If the connection is successful, the Text on button will become "Connected" . Moreover, notification will appear at the center of the screen. Before data was sent, users need to enter a file name in the File name box. Now, user can send various parameters to the potentiostat. In the text box will display hint for the order of data transmission which is arranged as follows: the pretreatment voltage, initial voltage, switching voltage, number of scan and scan rate. After all of parameter was sent, the application will wait to receive information from the potentiostat, then draw a graph and save data to a text file.

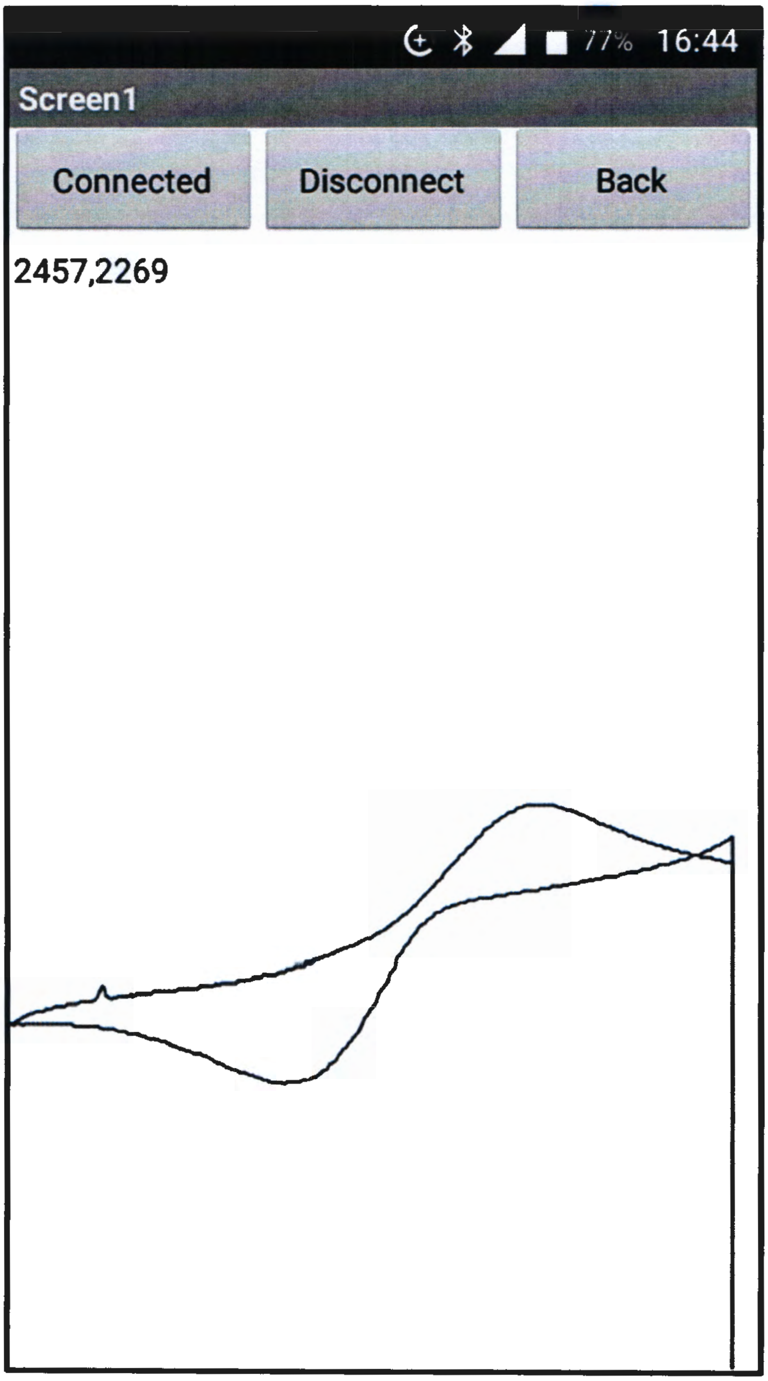

Figure 2.35 The screen to display the received data as a graph called a cyclic Voltammogram

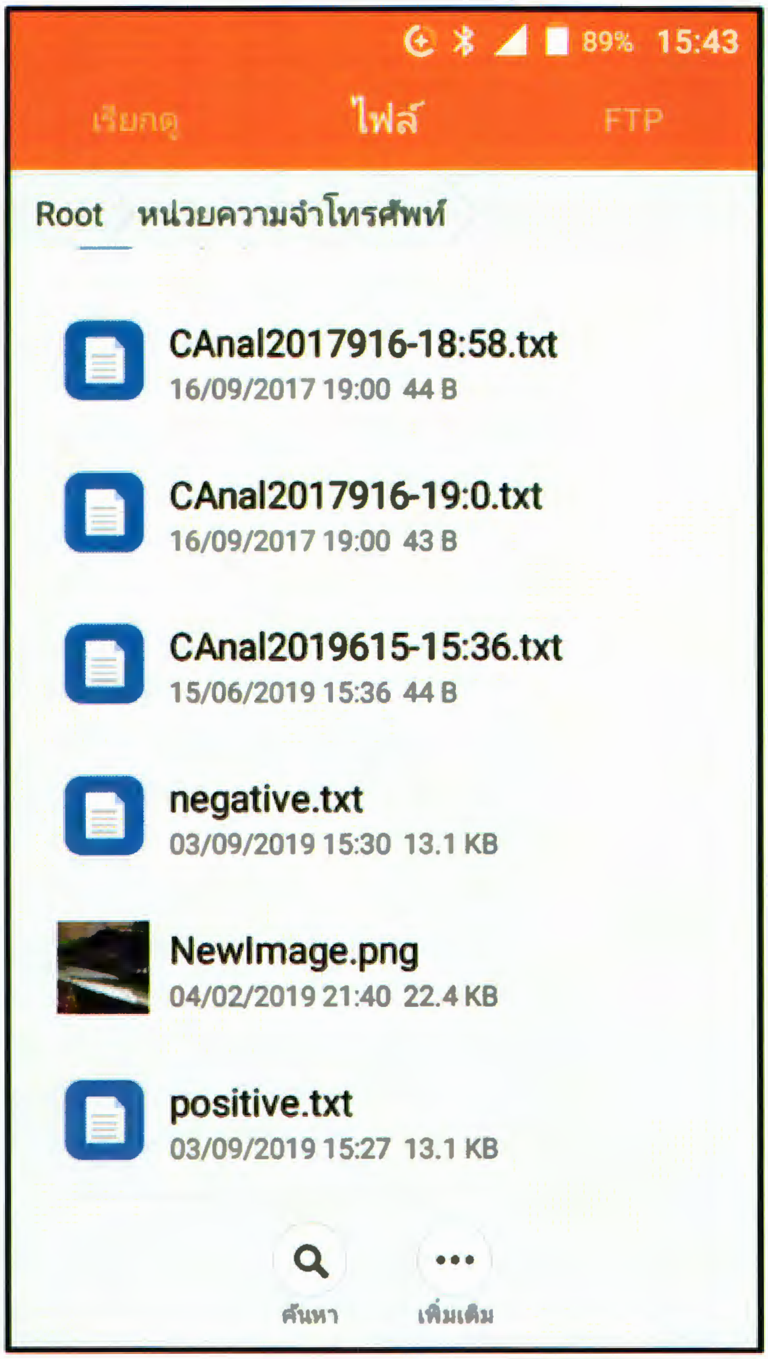

Figure 2.36 The data text file (.txt)

CHAPTER 3
ASSEMBLY OF THE POTENTIOSTAT AND PERFORMANCE TEST

The general system of electrochemical analysis consists of 3 main components as follows : the electrochemical cell, device for input voltage control and output signal detection called potentiostat and the recording system. As we mentioned in chapter 2 about the development of various components of potentiostat, so in this chapter we will talk about the combination of various components. In addition, the performance test of potentiostat when used together with the recording system that was developed in this project.

3.1 Assembly of the Potentiostat

The main component of the developed potentiostat consist of 4 mains as follows: Signal generator, Signal detector, Control amplifier and Current detector. The operation of the potentiostat was controlled by a microcontroller. Moreover, the microcontroller was also used to manage the communication between the potentiostat and the application on the smartphone. The assembly of potentiostat is shown in Figure 3.1.

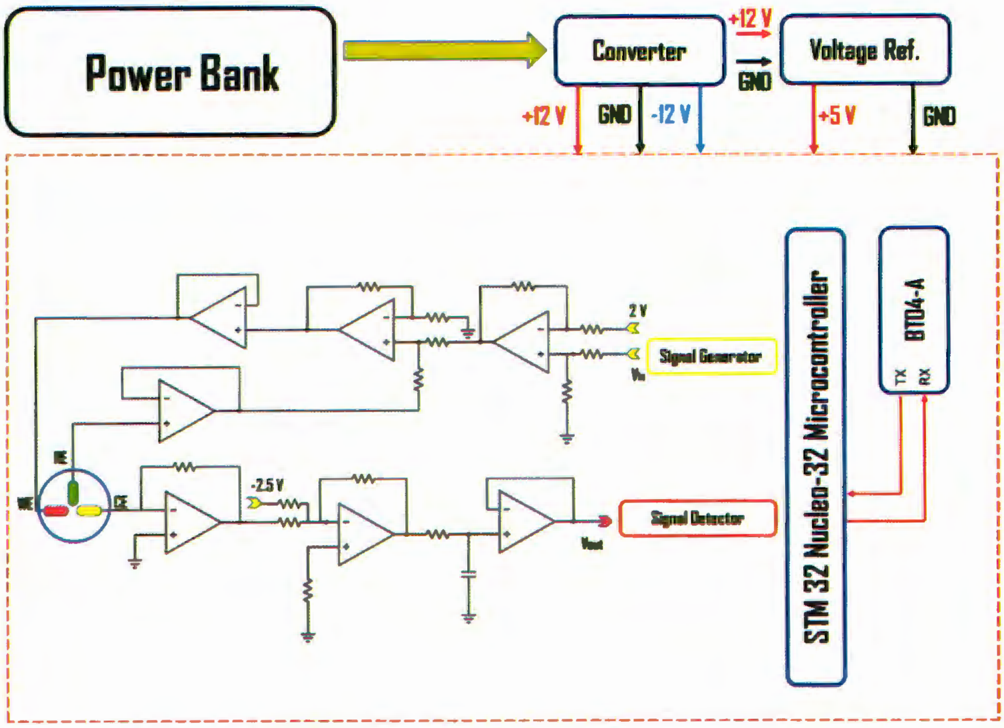

Figure 3.1 Potentiostat operation diagram

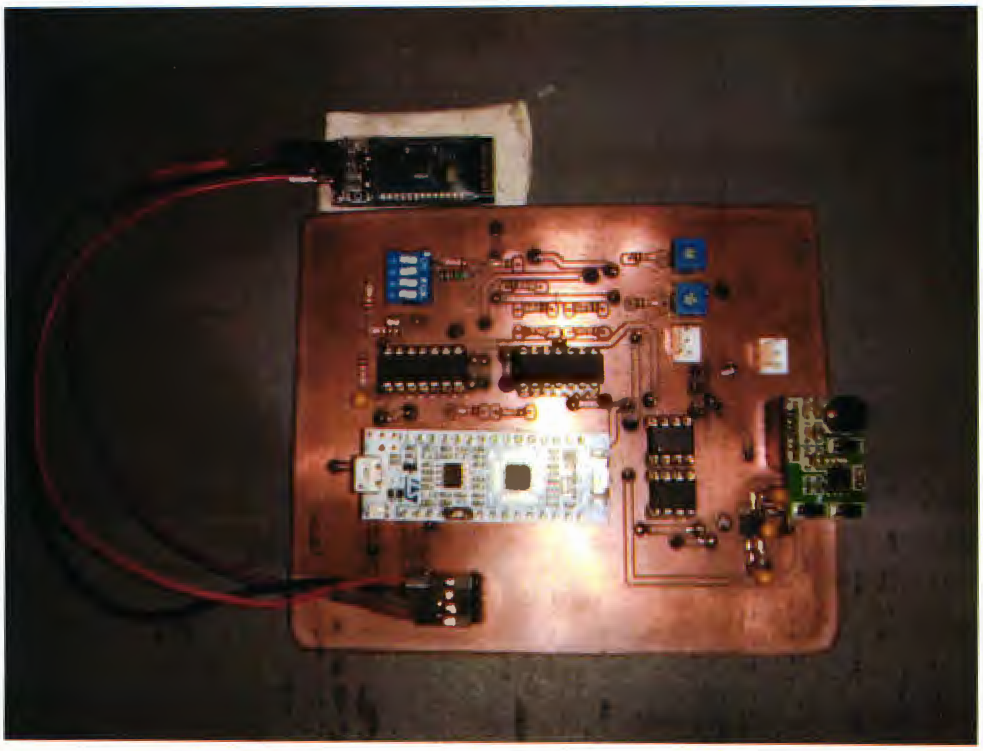

Figure 3.2 Picture of the completed Potentiostat design

The completed design shows the physical characteristic of device. The circuit was loaded on the printed circuit board (PCB) with size 10.0 x 12.0 cm^2. The circuit was covered with 15.0 x 15.0 x 7.0 cm^3 plastic box. On-off switch was placed on the front of the box. Moreover, there are also 3 cables for connecting to the electrodes which black cable, red cable and yellow cable will be connected to the reference electrode, working electrode and counter electrode, respectively. It should be note that the metal box or metal film liner inside the plastic box can be used in order to form a faraday cage to prevent possible electromagnetic interferences.

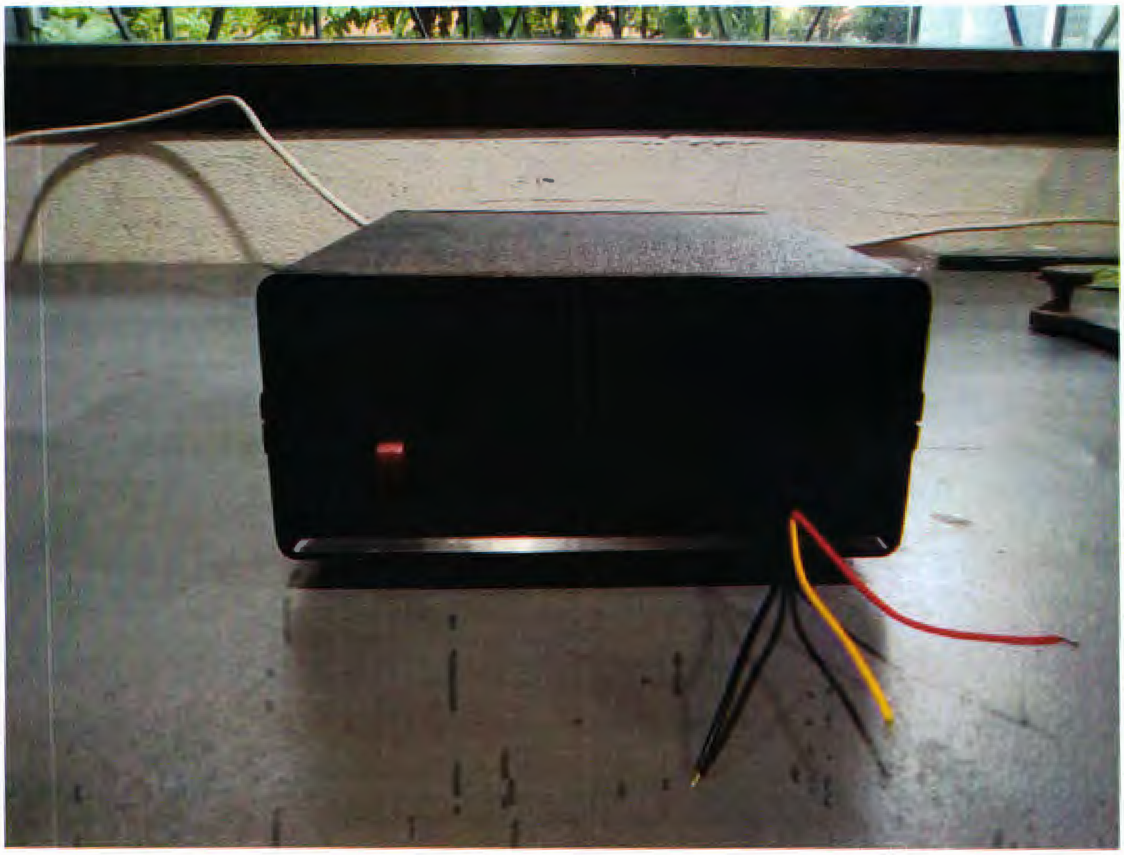

Figure 3.3 The potentiostat after packed inside the plastic box

3.2 Performance test

The developed potentiostat was tested with 3 conditions as follows : effect of scan direction, effect of scan-rate and effect of substance concentration. All 3 experiments will use potassium ferricyanide/ferrocyanide as a substance, Ag/AgCl as a reference electrode, stainless steel as a counter electrode and screen-printed carbon electrode

(SPCE) as a working electrode. The equipment setup for all 3 experiments is shown in Figure 3.4.

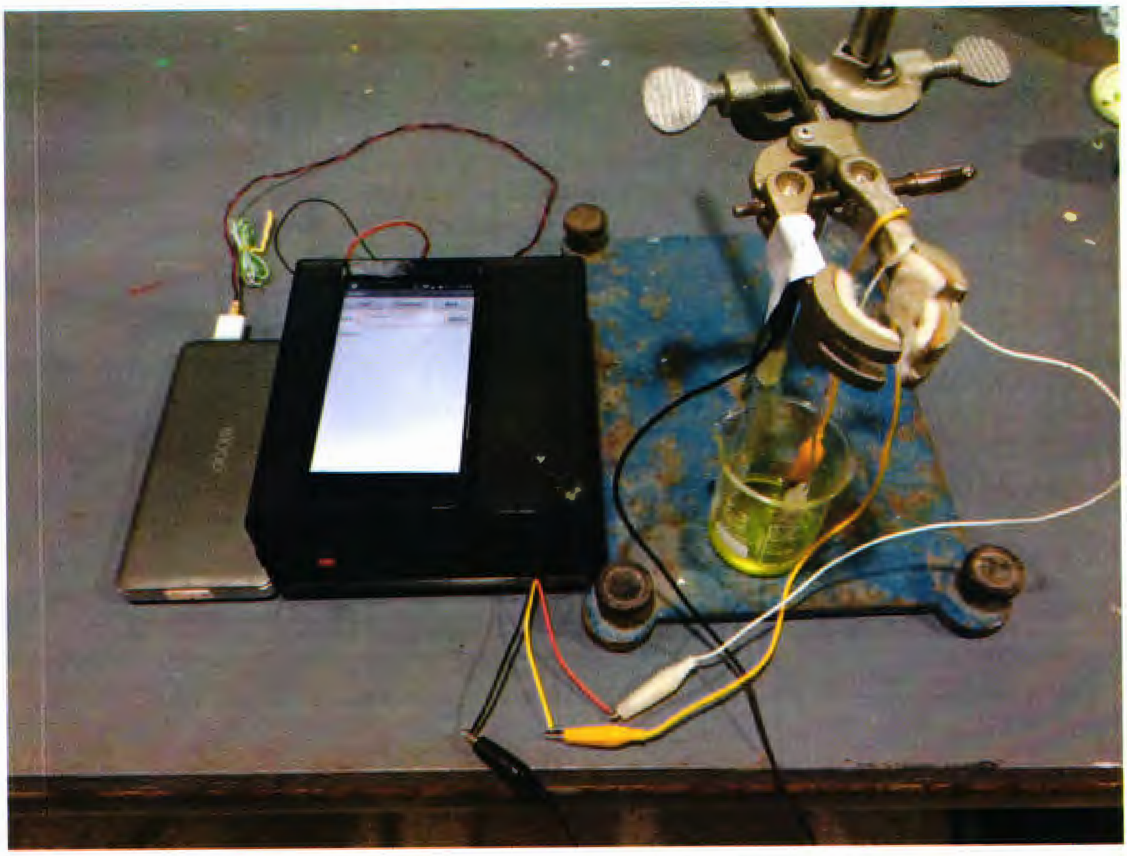

Figure 3.4 The equipment setup

3.2.1 Effect of scan direction

The experiment on the effect of scan direction was divided into 2 conditions. Firstly, the initial voltage was set as a positive voltage and the switching voltage was set as a negative voltage. Therefore, potentiostat will begin the experiment by providing more negative voltages into the electrochemical cell, this condition was called forward scan. After that, the signal will be scanned back become the cyclic. Secondly, the initial voltage was set as a negative voltage and the switching voltage was set as a positive voltage. Of cause, more positive voltage will be applied into the electrochemical cell, this condition was called backward scan. The experimental results of this part will indicate the stability of potentiostat in both directions.

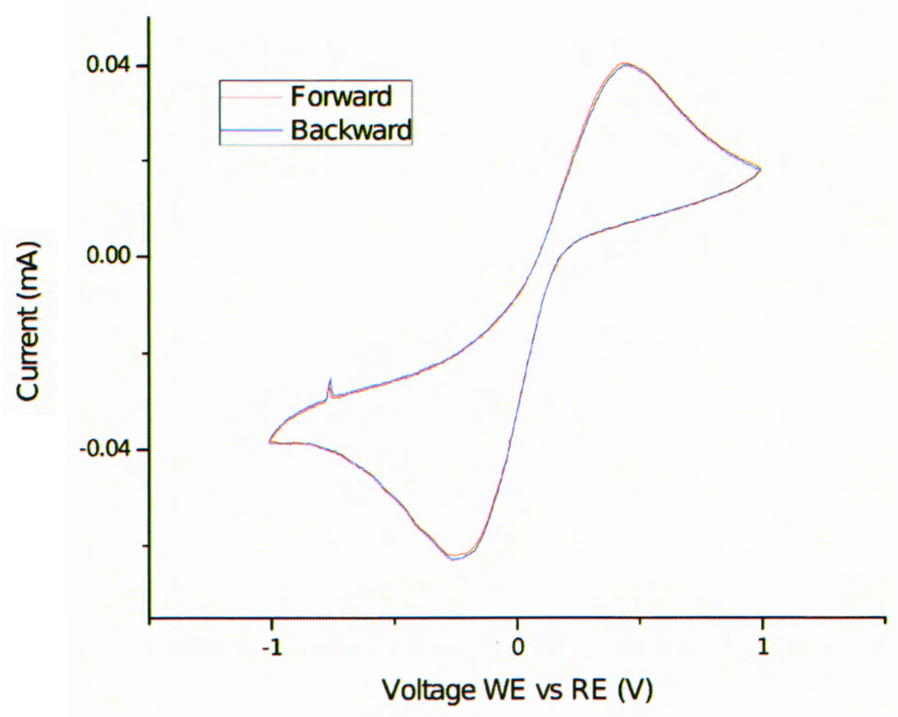

Figure 3.5 The experimental result about effect of scan direction

The experimental result show that the peak currents is from the positive and negative scans are nearly equal. From the result, it indicates a good stability of the developed potentiostat confirmed by less than 2% of percent different.

3.2.2 Effect of scan rate

To prove the capabilities of the potentiostat, a basic electrochemical experiment based on the redox reaction of potassium ferricyanide/ferrocyanide in water was performed. The diffusion coefficient of potassium ferricyanide was calculated by recording cyclic voltammetry experiments in a solution containing a known concentration of the substance for different scan rates and using the Randles-Sevick equation [26]. In this experiment, the 10 mM of potassium ferricyanide/ferrocyanide was prepared to use as a substance. The initial voltage was set at 1 V and switching voltage was set at -1 V. The developed potentiostat was tested by varying the scan rate values as follows : 10, 20, 30, 40, 50 and 60 mV/s.

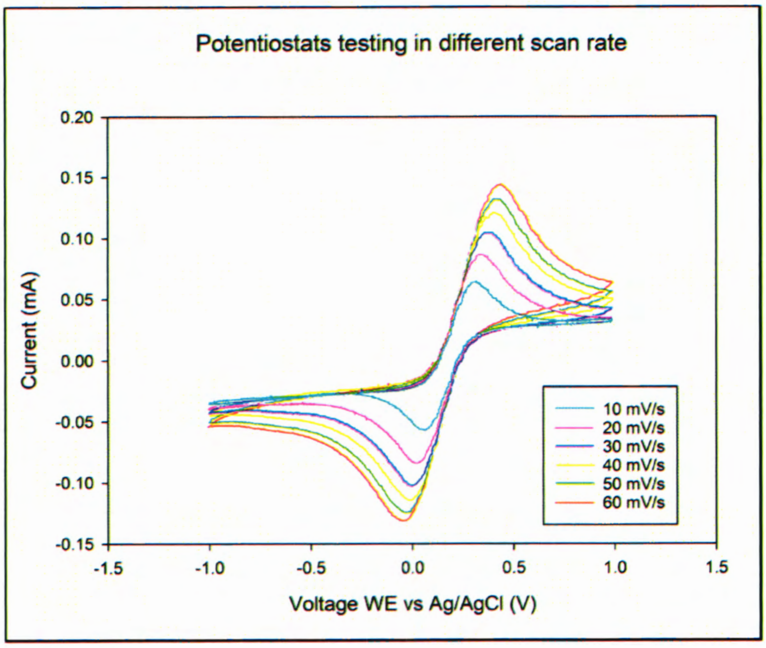

Figure 3.6 Cyclic voltammogram of potentiostat tested about effect of scan rate

Figure 3.6 indicates that the peak current of cyclic voltammogram corresponds to the scan rate. The cathodic and anodic currents plotted with the square root of the scan rate is shown in Figure 3.7.

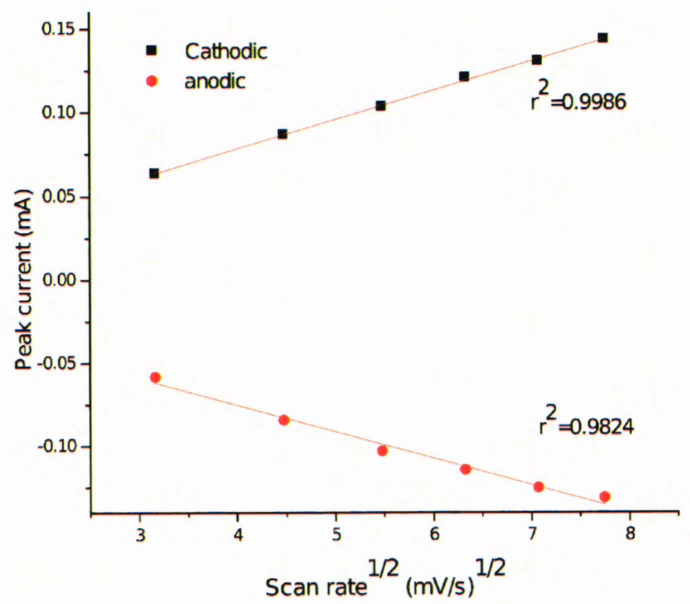

Figure 3.7 A plot of anodic and cathodic peak currents obtained from cyclic voltammograms versus square root of the scan rate

The dependence of redox peak current on the square root of scan rate demonstrates the good linearity of both the cathodic and anodic peak current which was confirmed by 0.9986 and 0.9824 of R-square value, respectively. The linearity of this graph points out a good detectability and good stability of the developed potentiostat for both the positive and negative detection. The linear relationship indicates that both the reaction is diffusion controlled reaction. From the slope of the linear fit and RandlesSevick equation, the diffusion coefficient of potassium ferricyanide is calculated to be 8.64 $\times 10^{-6}$ cm^2/s and 7.24 $\times 10^{-6}$ cm^2/s for cathodic and anodic peak currents, which is in good agreement with the value in the literature [27].

3.2.3 Determination of concentration of analyte (ferricyanide)

3.2.3.1 Sensitivity test

To test the sensitivity of the potentiostat, the electrochemical based on cyclic voltammetry was proceeded. The concentration of potassium ferricyanide is varied as follows : 0, 2, 5, 10, 20, 50, 100, 200, 300, 500, 1000, 2000 μM. The stimulus potential was swapped between 1 and −1 V with scan rates of 50 mV/s.

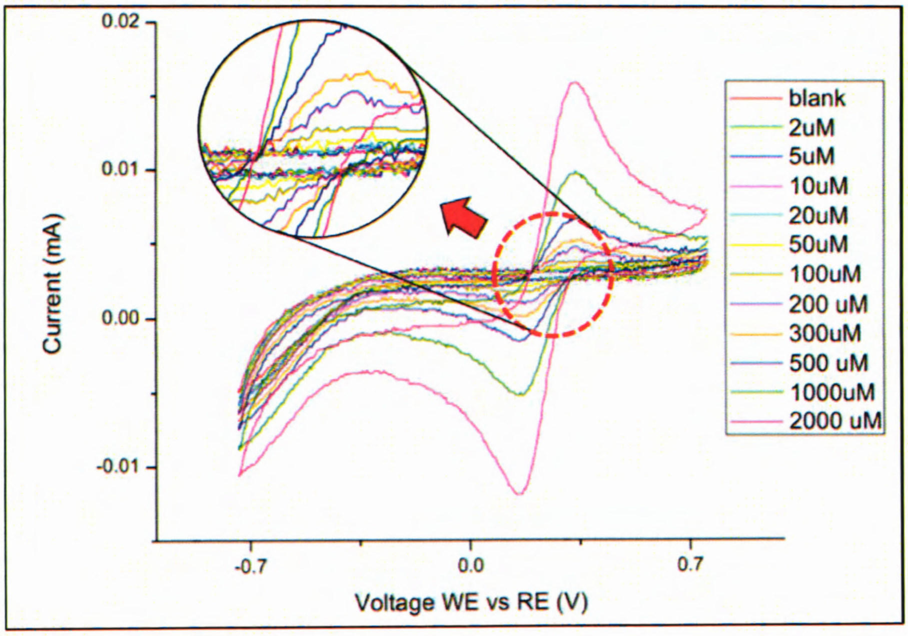

Figure 3.8 Cyclic voltammograms for the redox reaction of the ferricyanide at different concentrations for sensitivity test

Figure 3.8 shows the cyclic voltammograms of the varied concentration of potassium ferricyanide. This experiment points out the minimum current that potentiostat can detect is about 2 μA at 50 μM of substance concentration. Moreover, the results also show that when the concentration of potassium ferricyanide increase, the peak current was also increased which is agree with Randles-Sevick equation.

3.2.3.2 Accuracy test

From the previous experiment, we test the sensitivity of the developed potentiostat by using various concentration of ferricyanide. Also, the experiment based on concentration varying was performed in this part. The 2, 4, 6, 8, 10 mM of potassium ferricyanide were prepared to use as a substance. The voltage was determined as 1 V and -1 V of initial voltage and switching voltage, respectively. The scan rate value was set as 50 mV/s, the cyclic voltammogram used to perform the calibration curve between the concentration of potassium ferricyanide and cathodic peak current.

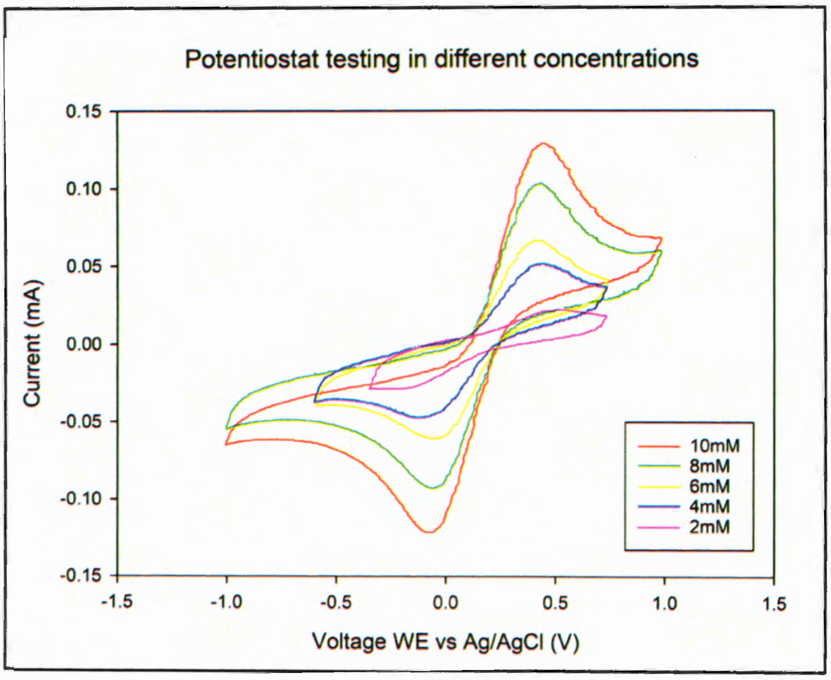

Figure 3.9 Cyclic voltammogram of the redox of ferricyanide at different concentrations for accuracy test

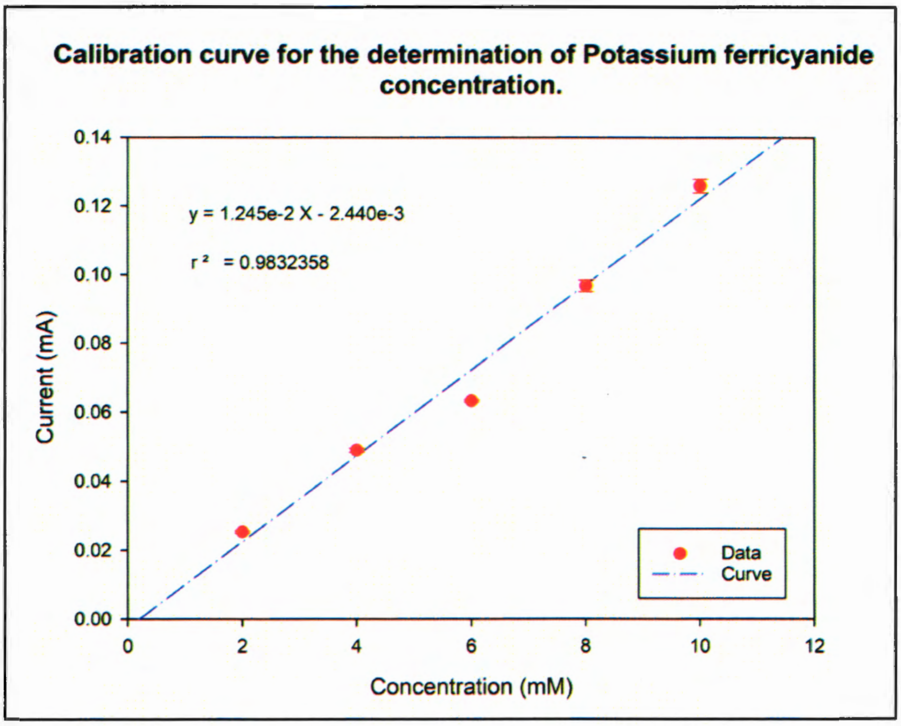

Figure 3.10 Calibration curve for the determination of potassium ferricyanide Concentration

The calibration curve in Figure 3.10. shows the linearity of data. To test the accuracy of this calibration curve, the experiment with the unknown concentration of potassium ferricyanide was prepared with a similar condition. The slope of the calibration curve was used to consider the concentration of the prepared sample.

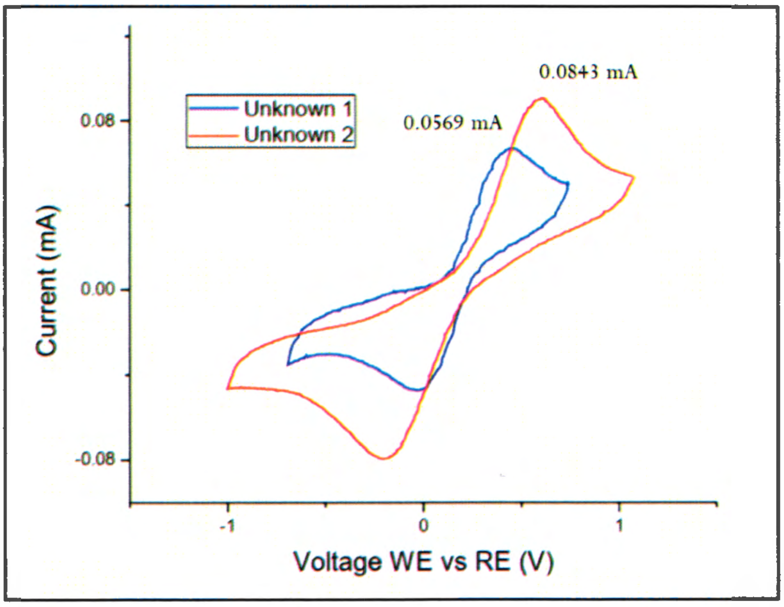

Figure 3.11 Cyclic voltammogram for the redox of the sample of unknow Concentrations

The results of cathodic peak current are 0.0569 mA and 0.0843 mA for unknown1 and unknown2 samples, respectively. When the results were analyzed to know concentration of samples by using the calibration curve equation, we found that the distinctions were less than 5%.The percentage error proved that the detection accuracy of developed potentiostat is quite well. So, this potentiostat could be used for electrochemical monitoring.

CHAPTER 4
CONCLUSION

Instrumentation for using in electrochemical analysis based on cyclic voltammetry has been investigated. The studies contain the design and fabrication of potentiostat and recording system used for cyclic voltammetry technique. This work aims to develop the potentiostat that low-cost and more compact compared with the commercial device. Moreover, we want to develop the portable recording systems. Potentiostat was developed by using STM 32 microcontroller to be the main controller unit. The component of potentiostat consist of the main unit as follows : the signal generator, control amplifier circuit, current detector and signal detector. The MCP4822, 12-bit digital to analog converter has been used as a signal generator. Because of the signal from the signal generator can't directly apply to electrochemical cell, so the control amplifier has been developed for signal optimization before applied to electrochemical cell . The current detector has been developed to detect current occurred from electrochemical reaction. However, the microcontroller cannot directly get the current, so after the current was detected, it was converted to voltage by using current to voltage converter circuit. The MCP3202, 12-bit dual channel analog to digital converter has been used as a signal detector. It has been used for detecting the output signal which is voltage converted from current. Moreover, voltage between working electrode and reference electrode has also been detected by the signal detector. After that, signal was converted from the analog signal to the digital signal. The detecting data has been sent to the recording system via Bluetooth signal. The BT04-A, Bluetooth module has been used for the communication between potentiostat and recording system. The recording system was developed in the form of application on the smartphone. The application was used to control various parameters for the experimental. In addition, it was used to display the cyclic voltammogram and save the data to text file. The text file can be exported to analyze and make a report later.

The results indicate that developed potentiostat can apply voltage to electrochemical cell in range of 2 to -2 V, 1 mV of resolution. The maximum current that can be detected is 0.25 and -0.25 mA for positive and negative current, respective. As expected, the potentiostat is low cost and more compact.

The performance of these was tested in various conditions as follow : the effect of scan direction, the effect of scan rate and the effect of concentration of an analyte by using potassium ferricyanide/ferrocyanide as a redox couple. The results show that the scan directions don't affect to the occurred peak current which confirm by 1% of the percentage difference of peak current. The result of varying scan rate indicates the cyclic voltammogram that the cathodic and anodic peak current increases according to the scan rate. The dependence of redox peak current on the square root of scan rate demonstrates the good linearity of both the cathodic and anodic peak current which was confirmed by 0.9986 and 0.9824 of R-square value, respectively. The diffusion coefficient of potassium ferricyanide is calculated to be 8.64×10^{-6} cm^2/s and 7.24×10^{-6} cm^2/s by using the slope of the linear fit and Randles-Sevick equation. The experimental based on varying concentration of substance was performed for a sensitivity and accuracy test. The results indicate the lowest peak current that can be detected is around 2 μA and -2 μA for positive and negative side. The sample concentration test was created to test the accuracy of the equipment. The experimental results show that the error percentage is less than 5%, which showed a fairly good performance of the developed potentiostat and recording system.

The comparison of the specification and performance of the developed potentiostat and some commercial potentiostat is summarized in Table 4.1.

Table 4.1 The specific and performance comparison between the developed potentiostat and some commercial potentiostat

	Developed potentiostat	EMstat³Blue	910 PSTAT mini
1. Voltage Range	±2 V	±3 V	±2.048 V
2.Apply Potential Resolution	1 mV	0.1 mV	1 mV
3.Current Measurement	2μA to 250 μA (2 range)	1 nA to 10 mA (8 range)	2 nA to 200 μA (6 range)
4. Dimension	15.0×15.0×7.0 cm³	10.0×6.0×2.7 cm³	8.0×5.4×2.3 cm³
5. Techniques	- Cyclic voltammetry	- Linear sweep voltammetry - Differential pulse voltammetry - Square wave voltammetry - Normal pulse voltammetry - Cyclic voltammetry	- Linear sweep voltammetry - Cyclic voltammetry - Square wave voltammetry - Differential pulse voltammetry
6. Communication	Bluetooth	Bluetooth and USB	USB
7. Price	2,000 THB	100,000 THB	109,800 THB

The suggestion of this study includes:

(1) The voltage range can be increased by adding an amplifier circuit [28] into the control amplifier circuit.

(2) Developer can improve an apply potential resolution by replacing a MCP4822, 12-bit digital to analog converter with 16-bit or 24-bit module.

(3) Sensitivity of current measurement (Current range) can be enhanced by increasing a resistant of feedback resistor in current to voltage converter circuit.

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APPENDICES

APPENDIX A

STM32 Nucleo-32 boards (MB1180)

STM32 Nucleo-32 boards (MB1180)

The STM32 Nucleo-32 boards based on the MB1180 reference board (NUCLEOF031K6, NUCLEO-F042K6, NUCLEO-F301K8, NUCLEO-F303K8, NUCLEOL011K4, NUCLEOL031K6, NUCLEO-L412KB, NUCLEO-L432KC) provide an affordable and flexible way for users to try out new concepts and build prototypes with STM32 microcontrollers, choosing from the various combinations of performance, power consumption and features. The Arduino TM Nano connectivity support makes it easy to expand the functionality of the Nucleo-32 open development platform with a wide choice of specialized shields.

The STM32 Nucleo-32 board is a low-cost and easy-to-use development kit used to quickly evaluate and start a development with an STM32 microcontroller in LQFP32 or UFQFPN32 package.

Before installing and using the product, accept the Evaluation Product License Agreement that can be found at www.st.com/epla.

For more information on the STM32 Nucleo-32 board and to access the demonstration software, visit the www.st.com/stm32nucleo webpage.

Features

(1) STM32 microcontrollers is in 32-pin packages.

(2) Three LEDs : USB communication LED (LD1), Power LED (LD2) and User LED (LD3)

(3) Reset push-button

(4) Board expansion connector : Arduino ™ Nano

(5) Flexible board power supply options : ST-LINK USB V_{BUS} and External sources

(6) On-board ST-LINK/V2-1 debugger/programmer with USB re-enumeration capability : mass storage, Virtual COM port and debug port

(7) Support of a wide choice of Integrated Development Environments (IDEs) including IAR™ EWARM, Keil MDK-ARM , GCC-based IDEs, Arm Mbed™

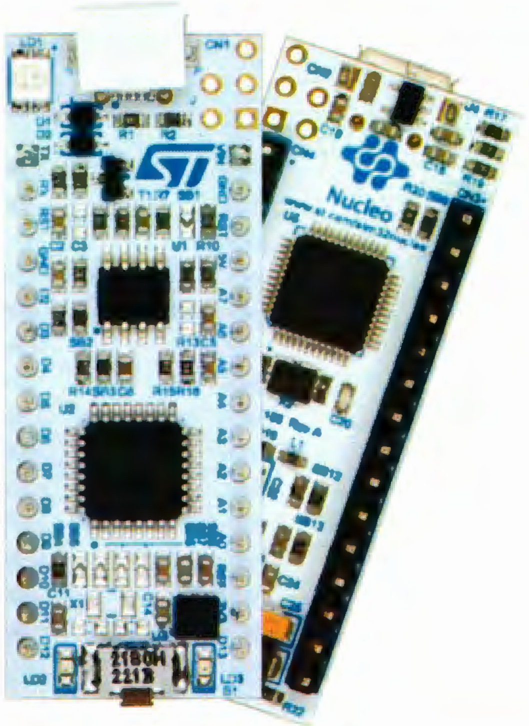

Figure A.1 STM32 Nucleo-32 board

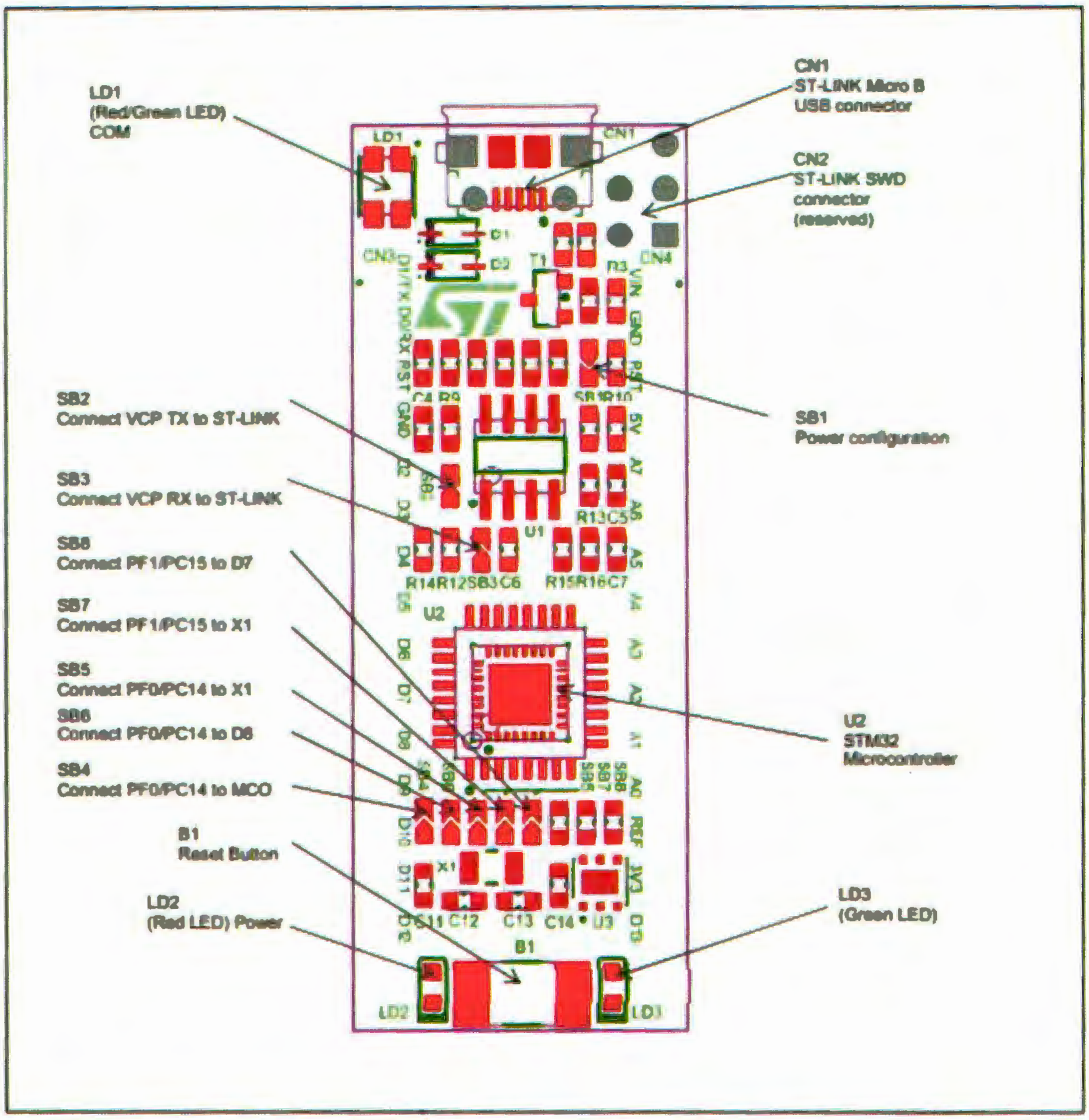

Figure A.2 STM32 Nucleo-32 board top layout

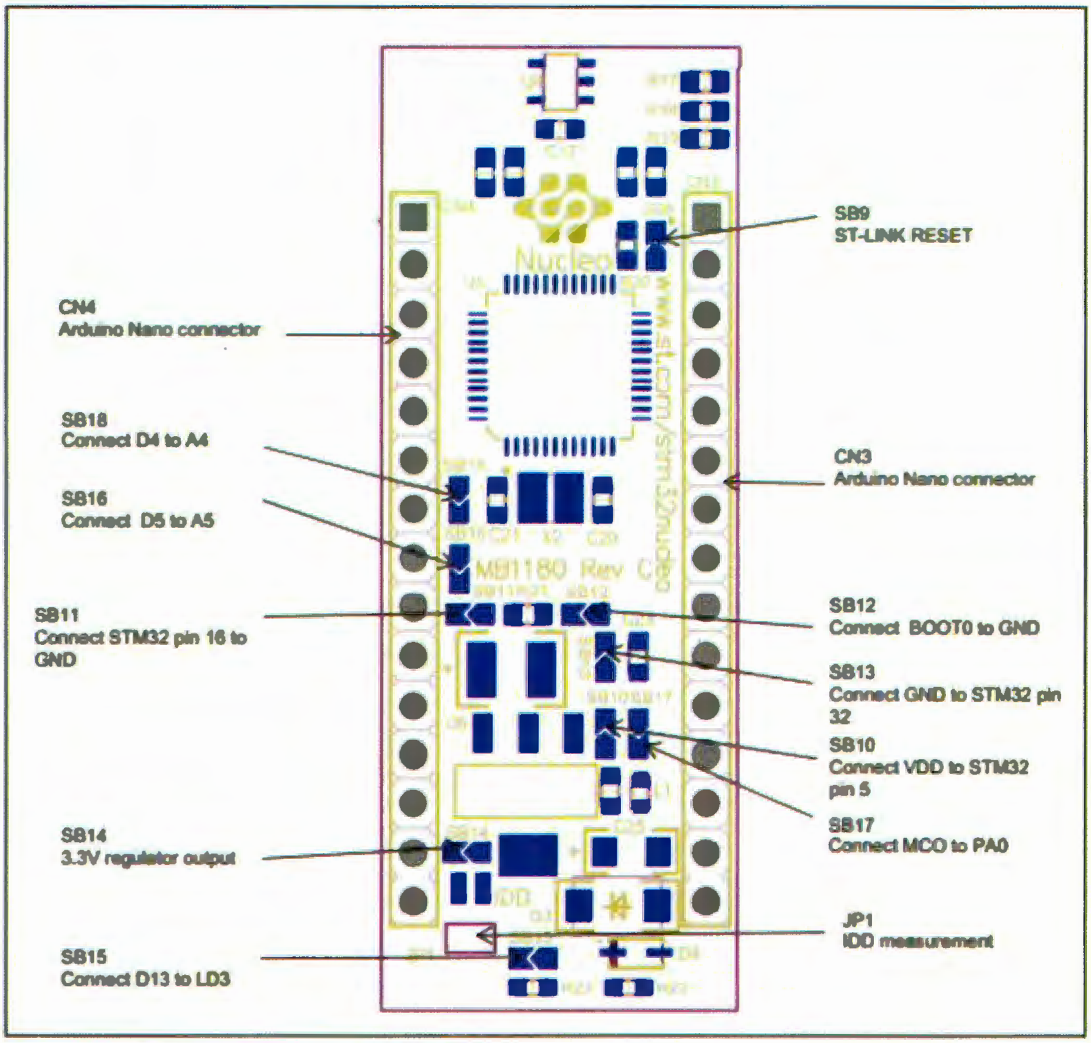

Figure A.3 STM32 Nucleo-32 board bottom layout

Connection

CN3 and CN4 are male connectors compatible with Arduino Nano standard. Most shields designed for Arduino Nano can fit the STM32 Nucleo-32 board.

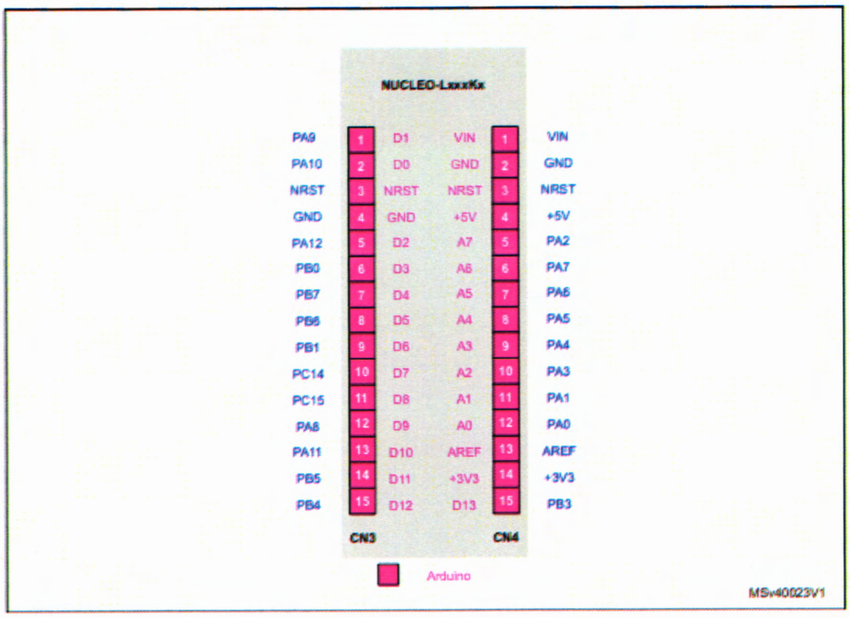

Figure A.4 Pin assignment

Table A.1 The connectors (Left connector) on NUCLEO-L432KC

Connector	Pin Number	Pin Name	STM32 Pin	Function
CN3	1	D1	PA9	USART_TX
	2	D0	PA10	USART_RX
	3	RESET	NRST	RESET
	4	GND	-	GROUND
	5	D2	PA12	-
	6	D3	PB0	TIM1_CH2N
	7	D4	PB7	
	8	D5	PB6	TIM16_CH1N
	9	D6	PB1	TIM1_CH3N
	10	D7	PC14	-
	11	D8	PC15	-
	12	D9	PA8	TIM1_CH1
	13	D10	PA11	SPI1_CS||TIM1_CH14
	14	D11	PB5	SPI1_MOSI||TIM
	15	D12	PB4	SPI1_MISO

Table A.2 The connectors (Right connector) on NUCLEO-L432KC

Connector	Pin Number	Pin Name	STM32 Pin	Function
CN4	1	VIN	-	POWER INPUT
	2	GND	-	GROUND
	3	RESET	NRST	RESET
	4	+5V	-	5V
	5	A7	PA2	ADC12_IN7
	6	A6	PA7	ADC12_IN12
	7	A5	PA6	ADC12_IN11||I2C_SCL
	8	A4	PA5	ADC12_IN10||I2C_SDA
	9	A3	PA4	ADC12_IN9
	10	A2	PA3	ADC12_IN8
	11	A1	PA1	ADC12_IN6
	12	A0	PA0	ADC12_IN5
	13	AREF	-	AVDD
	14	+3V3	-	3.3 V
	15	D13	PB3	SPI1_SCK

Getting started

Follow the sequence below, to configure the STM32 Nucleo-32 board and launch the demonstration software.

(1) Check solder bridge position on the board, SB1 OFF, SB14 ON (internal regulator), JP1 ON (IDD) selected.

(2) For a correct identification of all device interfaces from the host PC and before connecting the board, install the Nucleo USB driver, available at the www.st.com/stm32nucleo webpage.

(3) To power the board connect the STM32 Nucleo-32 board to a PC through the USB connector CN1 with a USB cable Type-A to Micro-B. The red LED LD2 (PWR) and LD1 (COM) light up and green LED LD3 blinks.

(4) Remove the jumper placed between D2 (CN3 pin 5) and GND (CN3 pin 4).

(5) Observe how the blinking frequency of the green LED LD3 changes, when the jumper is in place or when it is removed.

(6) The demonstration software and several software examples on how to use the STM32 Nucleo-32 board features, are available at the www.st.com/stm32nucleo webpage.

(7) Develop an application using the available examples.

APPENDIX B

High Precision Operation Amplifier (OPAx277)

High Precision Operation Amplifier (OPAx277)

The OPA277 series precision op amps replace the industry standard OP-177. They offer improved noise, wider output voltage swing, and are twice as fast with half the quiescent current. Features include ultra-low offset voltage and drift, low bias current, high common mode rejection, and high power supply rejection. Single, dual, and quad versions have identical specifications for maximum design flexibility.

OPA277 series op amps operate from ±2V to ±18V supplies with excellent performance. Unlike most op amps which are specified at only one supply voltage, the OPA277 series is specified for real-world applications; a single limit applies over the ±5V to ±15V supply range. High performance is maintained as the amplifiers swing to their specified limits. Because the initial offset voltage (±20μV max) is so low, user adjustment is usually not required. However, the single version (OPA277) provides external trim pins for special applications.

OPA277 op amps are easy to use and free from phase inversion and overload problems found in some other op amps. They are stable in unity gain and provide excellent dynamic behavior over a wide range of load conditions. Dual and quad versions feature completely independent circuitry for lowest crosstalk and freedom from interaction, even when overdriven or overloaded.

Single (OPA277) and dual (OPA2277) versions are available in DIP-8, SO-8, and DFN-8 (4mm x 4mm) packages. The quad (OPA4277) comes in DIP-14 and SO-14 surface-mount packages.

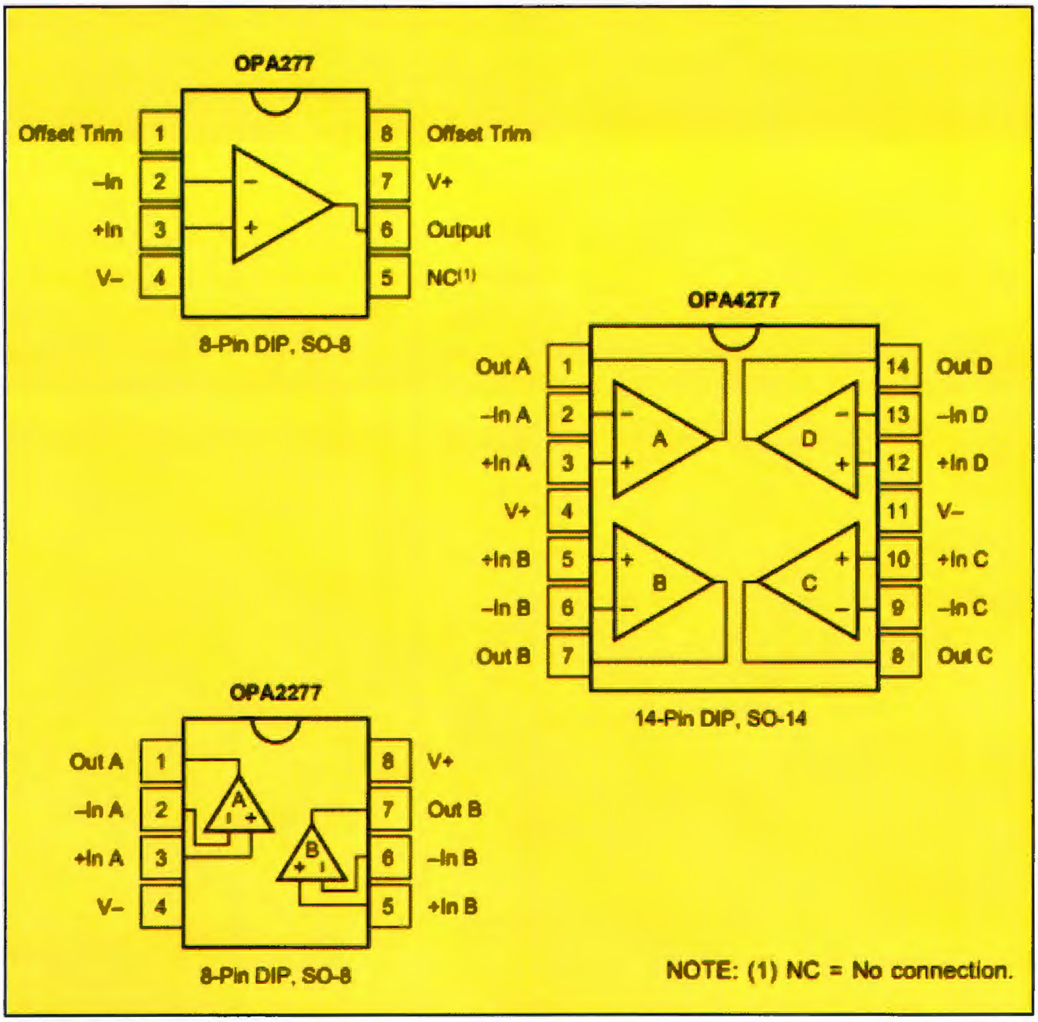

Figure B.1 OPAx277 Pin descriptions

Features

(1) Ultra Low Offset Voltage : 10 μV

(2) Low Bias Current: 1 nA max

(3) Wide Supply Range : ±2 V to ±18 V

(4) Low Quiescent Current: 800 μA/amplifier

(5) Single, Dual, and Quad Versions

Application

(1) Transducer Amplifier

(2) Bridge Amplifier

(3) Temperature Measurements

(4) Strain Gage Amplifier

(5) Precision Integrator

(6) Battery Powered Instruments

(7) Test Equipment

APPENDIX C

SPP-CA Bluetooth Serial Pass-through Module BT04-A

SPP-CA Bluetooth Serial Pass-through Module BT04-A

SPP-CA Bluetooth module is for intelligent wireless data transfer and build, follow V2.1 + EDR Bluetooth specification. The module supports UART interface, and supports Bluetooth SPP serial protocol, low cost, small size, low power consumption, the transceiver sensitivity advantages, just with a few external components will be able to achieve its powerful features.

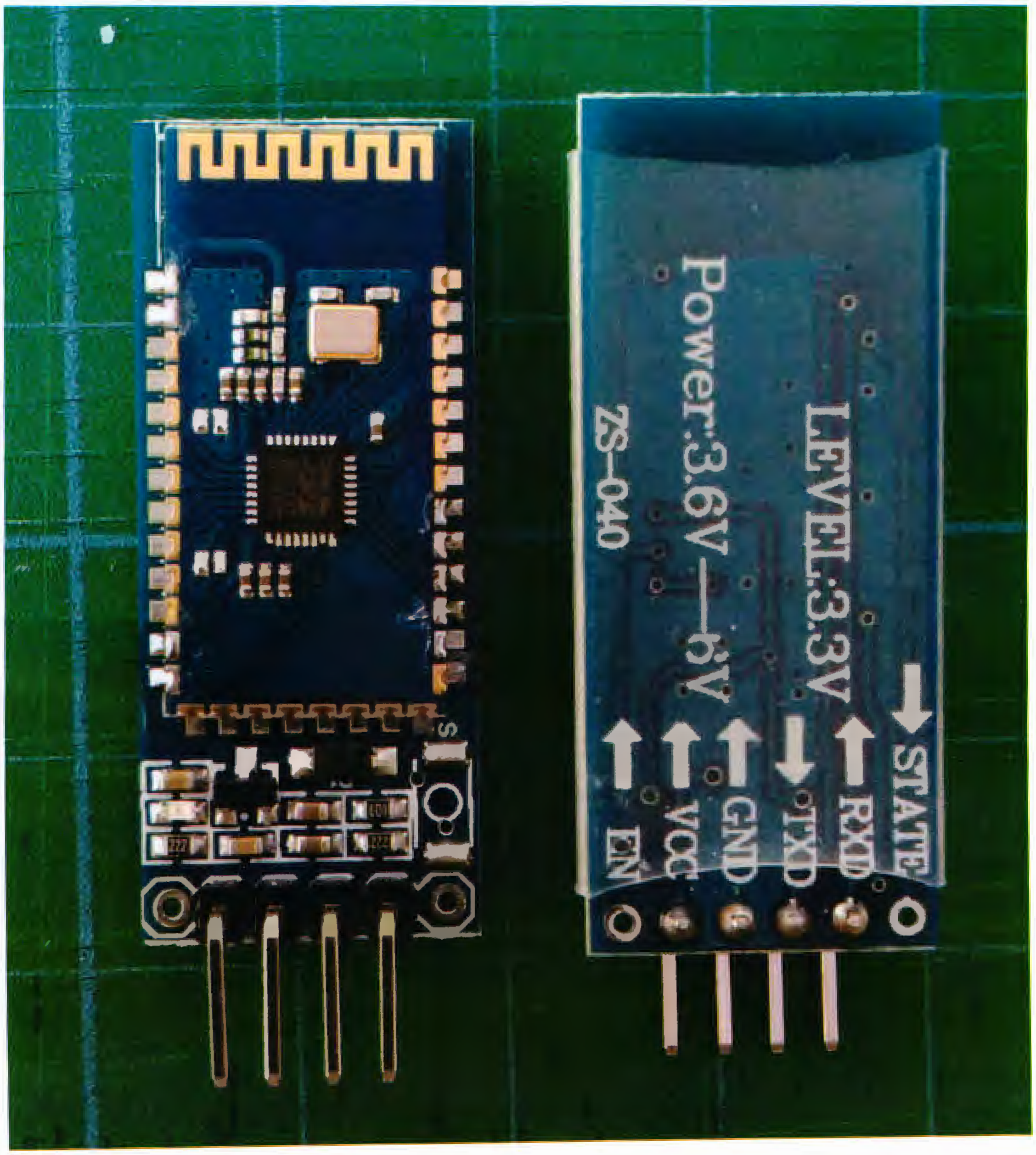

Figure C.1 Bluetooth Module BT04-A

Parameters

(1) Bluetooth V2.1 + EDR

(2) Bluetooth Class 2

(3) Built- PCB RF antenna

(4) Support UART interface

(5) 3.3 V power supply

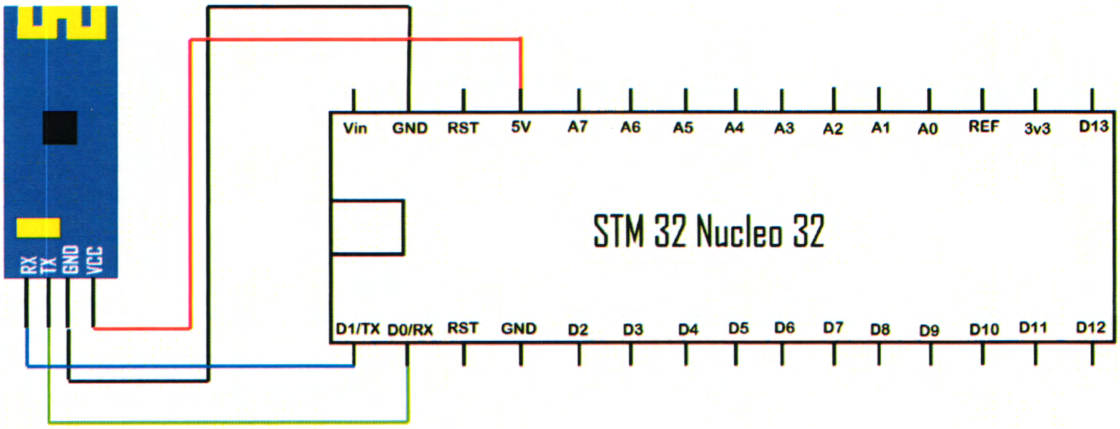

Figure C.2 Circuit diagram of BT04-A

APPENDIX D

REF50xx, Low-Noise, Very Lotaw Drift and Precision Voltage Reference

REF50xx, Low-Noise, Very Low Drift and Precision Voltage Reference

The REF50xx is a family of low-noise, low-drift, very high precision voltage references. These references are capable of both sinking and sourcing current, and have excellent line and load regulation. Table D.1 shows output voltage of each model of REF50xx.

Table D.1 Device Comparison Table

Model	Output Voltage
REF5020	2.048 V
REF5025	2.5 V
REF5030	3 V
REF5040	4.096 V
REF5045	4.5 V
REF5050	5 V
REF5010	10 V

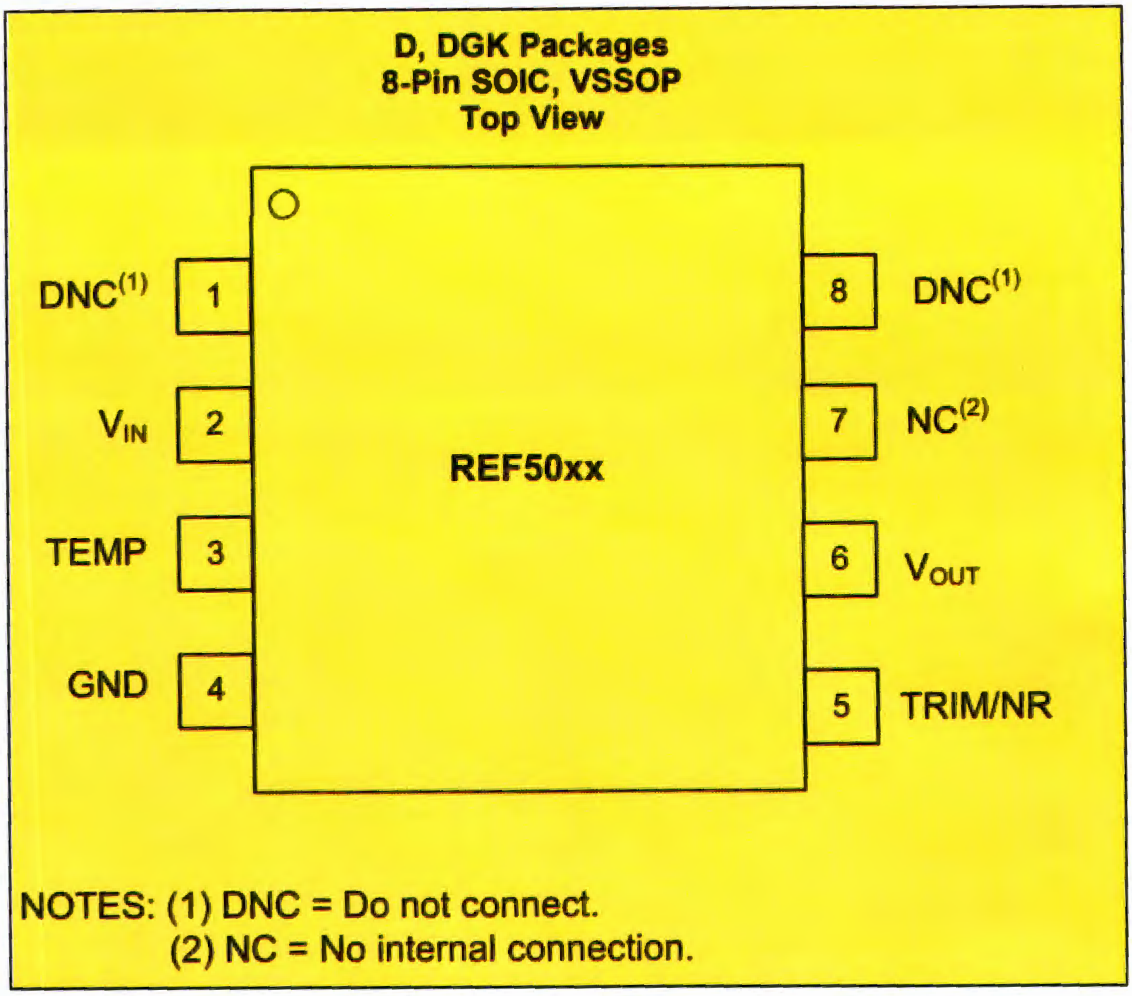

Figure D.1 REF50xx pin description

Table D.2 Pin Functions of REF50xx

PIN		DESCRIPTION
NAME	NO.	
DNC	1	Do not connect
VIN	2	Input supply voltage
TEMP	3	Temperature monitoring pin. Provides a temperature dependent output voltage
GND	4	Ground
TRIM/NR	5	Output adjustment and noise reduction pin
VOUT	6	Reference voltage output
NC	7	No internal connection
DNC	8	Do not connect

Basic Connections

Figure 40 shows the typical connections for the REF50xx. TI recommends a supply bypass capacitor ranging from 1 μF to 10 μF. A 1-μF to 50-μF output capacitor (CL) must be connected from VOUT to GND. The equivalent series resistance (ESR) value of CL must be less than or equal to 1.5 Ω to ensure output stability. To minimize noise, the recommended ESR of CL is from 1 Ω and 1.5 Ω.

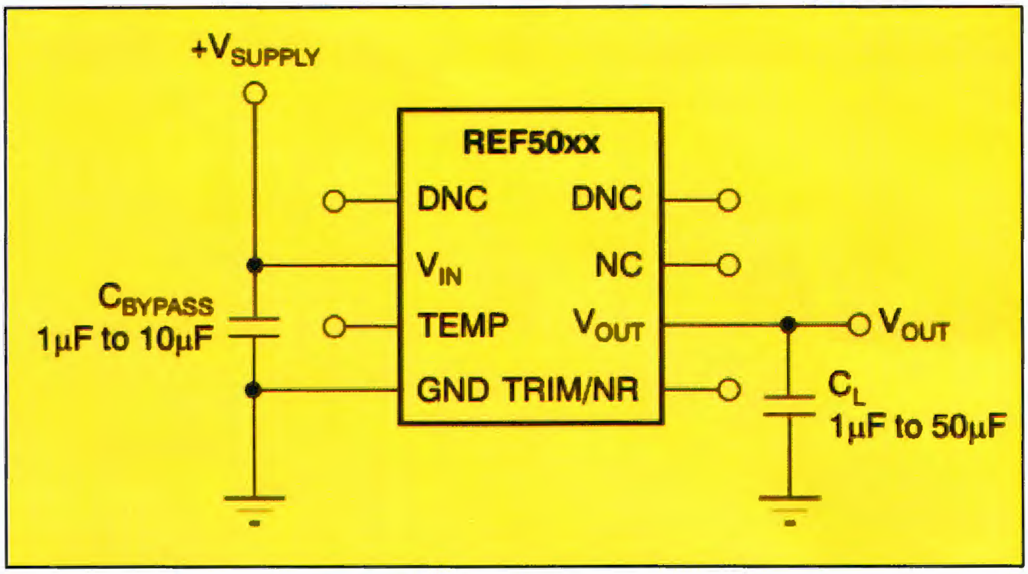

Figure D.2 REF50xx Basic Connections

Application

(1) Precision Data Acquisition Systems

(2) ATE Equipment

(3) Industrial Process Controls

(4) Medical Instrumentation

(5) Pressure and Temperature Transmitters

(6) Seismic monitoring syste

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