ISSN: 0975-833X

Available online at http://www.journalcra.com

International Journal of Current Research
Vol. 9, Issue, 05, pp.51072-51075, May, 2017

INTERNATIONAL JOURNAL
OF CURRENT RESEARCH

RESEARCH ARTICLE

DEVELOPMENT OF A CYCLIC VOLTAMMETRY SYSTEM BY DESIGNING A LOW COST POTENTIOSTAT

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ARTICLE INFO

Article History:
Received 25th February, 2017
Received in revised form
21st March, 2017
Accepted 14th April, 2017
Published online 31st May, 2017

Key words:

Cyclic Voltammetry, Potentiostat,
Op-amp, Microcontroller.

ABSTRACT

Cyclic voltammetry (CV) is a potentiodynamic electrochemical measurement in which working electrode's potential is ramped in the opposite direction to return to its initial potential. Potentiostat is an electronic hardware that controls the three electrode cell by maintaining the voltage between working electrode and reference electrode constant by adjusting the current at a counter electrode. Though now a day, many manufacturers are developing potentiostats having high accuracy and resolution, but the high cost is the obstruction. We have developed a low cost, portable CV system by designing a low cost and low component count potentiostat. TL054 op-amp and Arduino Mega 2560 microcontroller board is used to build a system. The developed system has been tested and showed the successful working.

Citation: Joshi, P. S., Relekar, A. S. and Sutrave, D. S. 2017. "Development of a cyclic voltammetry system by designing a low cost potentiostat", *International Journal of Current Research*, 9, (05), 51072-51075.

INTRODUCTION

Electrochemistry is defined as the branch of chemistry that examines the phenomena resulting from combined chemical and electrical effects. The branch of electrochemistry known as voltammetry is developed from the discovery of polarography. Currently there are various forms of voltammetry such as Polarography, Cyclic Voltammetry, Normal Pulse Voltammetry (NPV), Differential Pulse Voltammetry (DPV), Square-Wave Voltammetry (SWV), Anodic Stripping Voltammetry, Cathodic Stripping Voltammetry, Adsorptive Stripping Voltammetry, etc which are used for different analytical purposes. In all these techniques, the potential is applied and current is measured but slight difference is the way and timing for applying potential. Cyclic voltammetry (CV) has become a significant and broadly used electroanalytical technique in many areas of chemistry. It is generally used for the study of redox processes, in the analyses of electrochemical reactions between ions and surface atoms of electrodes under the investigation for understanding reaction intermediates for obtaining stability of reaction products, for qualitative information on electrode reaction mechanisms, qualitative properties of the charge transfer reactions between electrolyte ions and electrons from the electrode surface (Princeton Applied Research; Wang, 2000; Nicholson and Shain, 1964). Thus it is a powerful technique to study the redox reaction which plays a key role for charge storage mechanism in the study of supercapacitor. Cyclic voltammetry, a three electrode electrochemical cell, is based on varying the applied potential at a working electrode in both forward and reverse directions (at some scan rate) while observing the current. This technique involves a linear and a cyclic variation of electrode potential between the working and reference electrodes within a potential window by measuring the current that flows between working and counter electrodes. Cyclic voltammetry (CV) is a potentiodynamic electrochemical measurement in which working electrode's potential is ramped in the opposite direction to return to its initial potential. Potentiostat is an electronic hardware that controls the three electrode cell by maintaining the voltage between working electrode and reference electrode constant by adjusting the current at a counter electrode. Potentiostat is used to run most electroanalytical experiments for investigating the mechanism of a redox reaction. In recent times, the interest in developing the potentiostat for various applications has been increased. Though numbers of companies are manufacturing potentiostat instruments that deliver high precision but they are at equally high cost. There manufacturers usually make available the software for data analysis, electrochemical cells and the electrodes. Due to high cost, these instruments are not easily reachable for academic reason or for preliminary research

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study. Also there are a number of low cost potentiostats which deliver low accuracy or resolution. So if the potentiostat is developed for specific purpose or function then the cost as well as complexity of the circuit can be reduced. In this paper, we present the development of cyclic voltammetry system by designing the potentiostat which can be used for the study of supercapacitors where cyclic voltammetry is considered as a very preliminary characterization.

Instrumentation

To develop a handy and cost effective cyclic voltammetry system with different scan rates are the specific aims of the work. Even if cost effective, the system must be able to set the system parameters i.e voltages scan range and scan rate, it should be able to monitor the current in the electrode, it should convert the current from analog to digital form and should have the recorded data available over USB to a computer for data analysis. The major goal of the work is to create a microcontroller based scanning system which can accept the given input voltage range (in both positive and negative directions) and record the corresponding change in current. This voltage is provided by potentiostat. Hence the main concern is to design a potentiostat having simple circuit with a low cost and low component count. The block diagram for cyclic voltammetry scanning system is shown in Figure 1.

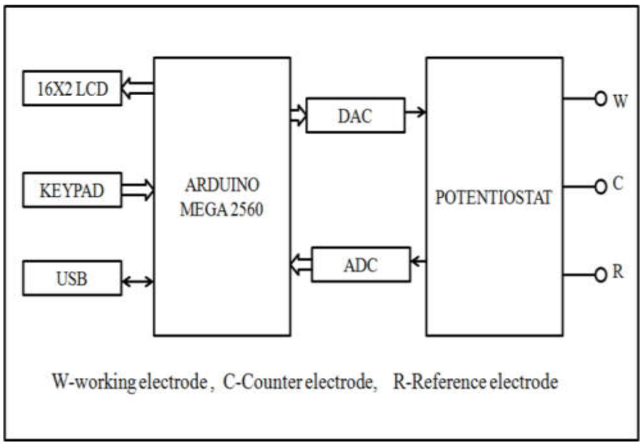

Figure 1. Block Diagram for Cyclic voltammetry Scan System

The potentiostat applies a known potential and monitors the corresponding change in current. It provides the staircase modulated potential in which there is a constant potential increment with steps. The advantage of such modulated signals is that every small change in capacitive current can be observed.ADC converts the analog value of the current into the digital value.DAC generates analog output. Microcontroller initiates all the commands to interface with other blocks and also performs the functions as to accept commands from keyboard, to set the system parameters, to drive LCD, to provide DAC digital data to generate output voltage. The value from ADC will be converted into appropriate data by microcontroller and stores the data into USB flash drive. Keypad is used to modify various settings, saves them and starts/stops the process. LCD displays the input parameters as Max and Min Voltage, Scan Rate, and important messages such as START, PROCESSING and END. USB flash drive stores the data that can be used for further analysis. An electrochemical cell is a sample holder consisting of an aqueous electrolyte and three electrodes – counter, reference and working.

Hardware

Figure 2. shows the functional block diagram of cyclic voltammetry system. Initially the data that is upper and lower threshold voltage values are entered through keypad. Microcontroller ARDUINO MEGA 2560 (http://www.atmel.com/Images/Atmel-2549-8-bit-AVR-Microcontroller-ATmega640-1280-1281-2560-2561_datasheet.pdf) accepts the data from keypad and generates the appropriate data in digital form for DAC. Here digital to analog converter AD 5761 is used. It converts the digital data into corresponding analog form (http://www.atmel.com/Images/Atmel-2549-8-bit-AVR-Microcontroller-ATmega640-1280-1281-2560-2561_datasheet.pdf).

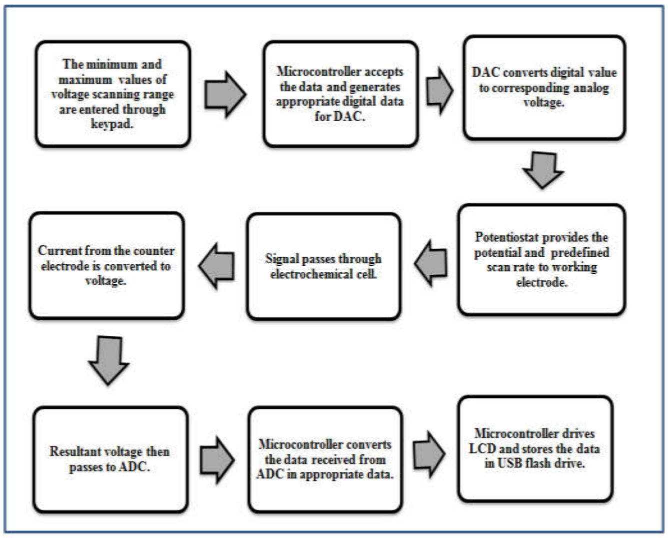

Figure 2. Functional Block Diagram for Hardware Methodology

Then the signal is given to potentiostat. Potentiostat is a circuit composed of operational amplifiers TL054. The main function of potentiostat is to provide the potential window and scan rate (10mV/Sec/50 mV/Sec/100 mV/Sec) to the working electrode. The signal then passes through electrochemical cell consisting of working, counter, reference electrodes and electrolyte. A staircase modulated voltage with regular increase of 0.1 V voltage is provided. Preset voltage range is scanned. The current from counter electrode is converted to voltage by the transimpedence amplifier from potentiostat. The resultant voltage is then passed to analog to digital converter MCP 3551 (http://ww1.microchip.com/downloads/en/devicedoc/21950b.pdf). Microcontroller converts the data received from ADC into the appropriate form that is current and also drives the LCD and stores the data into USB flash drive. This stored data can be used for further analysis. Potentiostat consists of operational amplifiers as shown in Figure 3. The circuit has two parts. First part provides the necessary power supply or potential to working electrode. This is then fed back to the same through electrolyte and reference electrode.

This part is required for the following reasons:

- The amplifier in this stage protects the DAC output from loading.
- This keeps the DAC voltage non-distorted upto the working electrode end of potentiostat.
- The buffer stage at the working electrode end ensures that the potential at working and reference electrode remains equal.

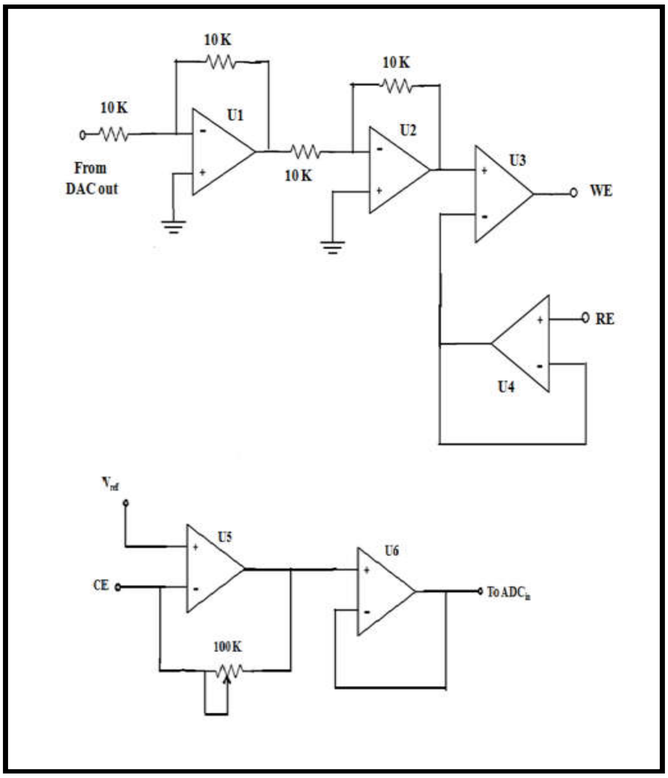

Figure 3. Simple Schematic of Potentiostat

This is the main and utmost required condition in cyclic voltammetry analysis and potentiostat design. Second part is Transimpedence amplifier. This stage converts the small amount of current through electrolyte into the voltage. The output of DAC is fed to inverting input of op-amp U1. Due to inverting amplifier configuration, this voltage is converted to negative equivalent voltage. This inverted voltage is then again inverted and initial voltage is obtained at the output of U2. In this way U1 and U2 forms a buffer amplifier. U3 and U4 are unity gain amplifiers. The feedback of this configuration is through the electrolyte, working electrode, reference electrode and U4. Due to unity gain configuration, the potential between working electrode and reference electrode is kept constant. For the purpose to avoid the loading effect, operational amplifier U4 is used. U5 is transimpedence amplifier which converts the current from counter electrode to the voltage. As the circuit generates bipolar voltages, a reference voltage is added at the transimpedence stage. This voltage shifter converts the bipolar voltage to unipolar voltage. The reference voltage is set to 2.5 V by adjusting POT. The operational amplifier U6 used is again in unity gain buffer configuration. This helps in reducing the loading effect and reading the non-distorted voltage measured. Loading effect is when the device at the output of any power supply tries to get more current than power supply can provide. This affects the voltage and the voltage decreases in order to keep the power at the output constant.

So when current increases, the voltage decreases. Now, the voltage from U6 is given to ADC. ADC reads the voltage and converts in digital form. Then microcontroller converts that voltage into current. The operational amplifier TL054 is designed to use with dual power supplies, high output current (http://www.ti.com/lit/ds/symlink/tl054.pdf). The advantage is there are 4 isolated op-amps in each package. This simplifies the circuitry and reduces the cost. The potentiostat circuit is composed of these operational amplifiers and used to process signal from DAC and feedback from reference electrode and convert the current from counter electrode to voltage. The DAC used here AD 5761 is a single channel, 16 bit serial input, voltage output, digital-to-analog converter. It uses a serial interface that operates at clock rates of upto 50 MHz and is compatible with DSP and microcontroller interface standards. The DAC will start its operation when the user will input the parameters required to run the sweeping voltage. DAC output amplifier is capable of generating both unipolar and bipolar voltages. Data is written to AD 5761 in a 24 bit word format via a 4 wire (SYNC, SCLK,SDI and SDO) digital interface that is SPI (Serial Peripheral Interface) compatible.

MCP 3551 device is 2.7 V to 5.5 V low power, 22 bit Delta-Sigma analog-to-Digital Converter. It provides high accuracy and low noise performance. Serial communication between microcontroller and ADC is achieved using CS, SCK and SDO/RDY. SCK synchronizes data communication with the device. SDO/RDY is the output data pin for the devices. CS gets all communication to the device and can be used to select multiple devices that share the same SCK and SDO/RDY pins. Keypad 4X4 is used for loading numeric into the microcontroller (https://www.parallax.com/sites/default/files/ downloads/27899-4x4-Matrix-Membrane-Keypad-v1.2.pdf). A 16X2 LCD is used to display the input parameters as well as the messages while processing the scan (https:// circuitdigest.com/article/16x2-lcd-display-module-pinout-datasheet). The CH376S USB read/write module has a CH376S chip onboard (http://arduinobasics.blogspot.in/ 2015/ 05/ch376s-usb-readwrite-module.html). The Arduino Mega is a microcontroller board based on the ATmega2560 (https://www.arduino.cc/en/Main/arduinoBoardMega2560). It has 54 digital input/output pins (of which 14 can be used as PWM outputs), 16 analog inputs, 4 UARTs (hardware serial ports), a 16 MHz crystal oscillator, a USB connection, a power jack, an ICSP header, and a reset button. It contains everything needed to support the microcontroller. Below ()Figure 4 is the photograph of developed CV system.

Figure 4. Photograph of developed CV System

RESULTS AND DISCUSSION

After testing the hardware, the cyclic voltammetry was carried out using an electrochemical cell consisting of metal oxide thin film as working electrode, Pt auxiliary electrode as counter electrode and a saturated Calomel electrode as reference electrode. For this Mn doped Ruthenium Oxide thin film was used as working electrode. The cyclic voltammetry was carried out in a potential window -0.8 V to 0.6 V for three different scan rates 10 mV/Sec, 50 mV/Sec and 100 mV/Sev in a 0.1 M KOH electrolyte. Here the voltage is stepped in 0.1 V upto final voltages. After completion of the predefined scan, the data is stored in USB flash drive and used for further analysis. The CV plot is shown in Figure 5.

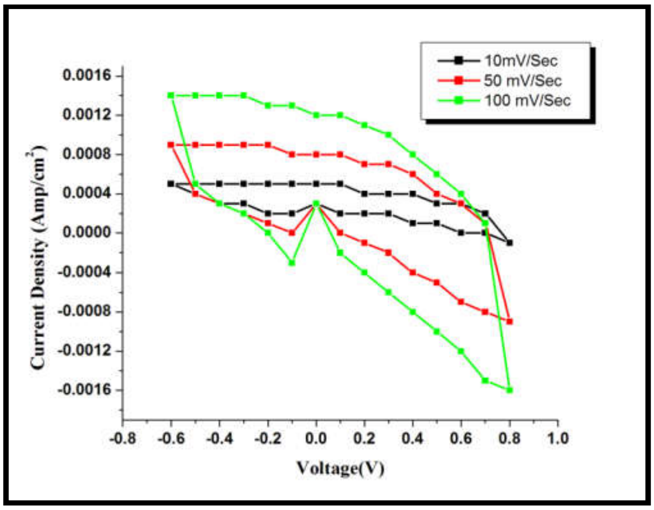

Figure 5. Cyclic voltammogram for Mn: RuO_2 thin film electrode from developed CV system

The data stored in USB was used for further analysis. The rectangular shape of CV curve showed the supercapacitive behaviour. Also the area under the curve was increased with increase in scan rate which in turn decreased the specific capacitance. Our system showed the similar results as the laboratory tests. The calculated specific capacitance values were 262 F/g, 149 F/g and 124 F/g for 10, 50 and 100 mV/Sec scan rate respectively. These values are comparatively less than the laboratory test values. In laboratory the similar test was conducted using the same sample by CH electrochemical workstation. The decrease in values may be due to low resolution and sophistication. The sophistication may be of different levels. First may be about the microcontroller used, secondly about component sophistication and third can be signal conditioning and board creation. Due to these limitations there may be difference in results.

Conclusion

The system has achieved the initial Specific aims. The system is able to present a working potentiostat which is capable of performing cyclic voltammetry according to user-inputted parameters. The system has been able to accept the voltage in both directions, generates the step voltage increase of 0.1 V, measures the corresponding current and stores the data in USB flash drive which can be used for analysis. Simultaneously, the system is able to display the input variables, start and end of the process. It is able to run the scan at three different scan rates 10 mV/Sec, 50 mV/Sec and 100 mV/Sec. The results obtained show the rectangular shape of voltammogram giving supercapacitive behaviour. Successful scanning in both positive and negative voltage windows, generation of satisfactory and bipolar current, increase in current density, increase in area under the curve and decrease in specific capacitance with increase in scan rate are seen from results. The similar observations are seen as compared to laboratory tests.

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