Embedded 32-bit Differential Pulse Voltammetry (DPV) Technique for 3-electrode Cell Sensing

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Abstract

This paper addresses the development of differential pulse voltammetry (DPV) embedded algorithm using an ARM cortex processor with new developed potentiostat circuit design for in-situ 3-electrode cell sensing. This project is mainly to design a low cost potentiostat for the researchers in laboratories. It is required to develop an embedded algorithm for analytical technique to be used with the designed potentiostat. DPV is one of the most familiar pulse technique method used with 3-electrode cell sensing in chemical studies. Experiment was conducted on 10mM solution of Ferricyanide using the designed potentiostat and the developed DPV algorithm. As a result, the device can generate an excitation signal of DPV from 0.4V to 1.2V and produced a peaked voltammogram with relatively small error compared to the commercial potentiostat; which is only 6.25% difference in peak potential reading. The design of potentiostat device and its DPV algorithm is verified.

Keywords - differential pulse voltammetry (DPV), potentiostat

1. Introduction

Over the past few decades, electrochemical devices have been developed and used broadly in industrial, biotechnology, physics and chemistry laboratories to help the researchers conduct their experiments. Researchers use these instruments to process the required sample collection and make analysis on the chemical reactions. Potentiostat is one of the most important hardware in electrochemical instruments. It is normally used with 3 kinds of electrode known as working electrode(WE), reference electrode(RE) and counter electrode(CE) as its sensing cell. Potentiostat is used to control the voltage difference between a working electrode and reference electrode in electrochemical cell. It also measures the current flow between the working electrode and counter electrode. Although this instrument is an important element in electrochemical research, they have seen relatively little application in resource poor settings, such as undergraduate laboratory courses and the developing world due to the cost factor. Hence, it is required to develop a device that can overcome this circumstances.

Most of the researchers focus on the analog design of the potentiostat [1],[2],[3], but very few discussing about the development of its software algorithm for 3-electrode cell sensing[4]. In this paper, the DPV-based embedded to allow in-situ 3-electrode cell sensing is discussed.
DPV is one of the frequently used voltammetry techniques [5],[6],[7] for detecting analytes in flow systems, including the in vivo analysis of a patient’s blood and DNA. Furthermore, DPV is suitable for the rapid analysis of a single analyte. In DPV, the current is sampled twice in each pulse period and the difference between these two current values is recorded to produce a peaked voltammogram. The height peak is directly proportional to the concentration of analyte. DPV has benefit over the other analytical technique as it can reduce the effect of capacitive current and improves the signal-to-noise ratio by attenuating the background current[8]. Figure 1 shows the differential pulse voltammetry and its produced peaked voltammogram.

![Figure 1 DPV excitation signal potential and its voltammogram](image)

2. Materials and Method

2.1 Experiment Setup

The developed system is composed of an MCU component LPC1768, potentiostat and 3-electrode system. The LPC1768 is a 32-bit ARM Cortex-M3 based MCU for embedded applications. It is used to program the excitation signal voltage for potentiostat, measure and converting the analog to digital signal of the chemical response current and store the data to be analyzed. The electrochemical measurements is performed at room temperature by implementing the developed readout circuit and 3-electrode electrochemical system which consists of gold sheet with dimensions of 0.25x25x25mm as a working electrode, an Ag/AgCl as reference electrode (RE) and a platinum wire as counter electrode (CE). The differential pulse voltammetry (DPV) is performed in 40 mL of 10mM of ferricyanide. The experiment setup is shown in the figure 2.
The potentiostat will scan the excitation signal between RE and WE and provide the electrochemical reactions to produce a small current through WE and CE. The scan range is set from +0.4V to 1.2V with the scan rate of 0.01V/s. As the scanning reaches the reduction potential, the oxidization rate increased sharply, that raised the sensor current (Faradiac current) and causes a peak in the electrode current. Potentiostat measured this induced current, and after conversion to the voltage, it is sampled through the embedded 12-bit analog-to-digital converters (ADCs) and stored in the MCU memory to be analyzed.

### 2.2 Design of DPV Algorithms

DPV is a superposition of a staircase and pulse waveform, which the potential between the pulse is not returning back to the same rest potential. Figure 2 shows the flowchart on how the DPV is obtained. Firstly, the program initialize all the parameter values as required. DAC of the microcontroller will produce the excitation voltage and ADC will read the current reading. The parameter values of DPV excitation voltage are as shown in table 1. Theoretically, the pulse period must be set at least twice of the pulse width. The scan rate of DPV is determined by step potential/pulse period.

| Differential Pulse Voltammetry Parameters | Value |
|-------------------------------------------|-------|
| Initial Potential (V)                    | 0.4   |
| Final Potential (V)                      | 1.2   |
| Step Potential (V)                       | 0.005 |
| Pulse Width (s)                          | 0.25  |
| Pulse Period (s)                         | 0.50  |
| Pulse Amplitude (V)                      | 0.1   |
| Scan Rate (V/s)                          | 0.01  |
After the initial potential of 0.4V, the voltage is maintained for 0.25s before it increase to the pulse potential with the increment of 0.1V. Before the potential pulse is applied, the current reading is taken known as base current, I$_{\text{base}}$. The pulse potential is increased and maintained for 0.25s and before the pulse ends, the pulse current, I$_{\text{pulse}}$ is sampled. The difference of the two current responses (I$_{\text{pulse}}$-I$_{\text{base}}$) will give a point to produce a peaked voltammogram with the expected peak occured at 0.8V. The new cycle will add the potential from the previous base potential and again repeat the steps. The looping will stop once it reaches the final base potential of 1.2V.

![Flowchart of DPV](image.png)
3. Result and Discussion

To test the performance of the device and its software algorithm, the chemical experiments was conducted on 10mM of Ferricyanide. The result of the voltammogram produced from the electrochemical reaction will be compared with the available commercial potentiostat as a reference. Potential range measurement of the designed instrument is between 0.4V and 1.2V. Figure 3 shows the output from the DAC of the ARM Microcontroller which showing the DPV voltammetry technique as programmed based on the written algorithm. The programmed and actual values of the excitation voltage parameters is compared and the error percentage is shown in table 2. From the recorded data, the percentage error is very small which is only 1.4%. In terms of timing, the 32-bit embed gives a good response and gives less than 1% of error in completing the scanning time.

![Figure 4 Output of ARM Microcontroller showing DPV voltammetry technique as programmed based on the written algorithm](image)

| Parameters                  | Program | Actual | Percentage Error(%) |
|-----------------------------|---------|--------|---------------------|
| Initial Potential(V)        | 0.400   | 0.400  | 0                   |
| Final Potential(V)          | 1.210   | 1.210  | 0                   |
| Step Potential(V)           | 0.005   | 0.0051 | 1.4                 |
| Pulse Width(s)              | 0.25    | 0.25   | 0                   |
| Pulse Period(s)             | 0.50    | 0.50   | 0                   |
| Pulse Amplitude(V)          | 0.1     | 0.0991 | 0.88                |
| Scan Rate (V/s)             | 0.01    | 0.01   | 0                   |
| Completion Time of Scanning(s) | 80      | 80.63  | 0.78                |

To validate the developed system, the 3-electrode sensor is used with an authorized potentiostat, Autolab PGSTAT204 to perform electrochemical detection test on 10mM ferricyanide. The DPV parameters value is maintained as in the developed system. Figure 5 shows the graph plotted from the data collected in spreadsheet. As can be seen in the graph, the oxidation peak occur at the voltage of 0.8V when using the commercial potentiostat while the developed device produce the peak in the range of 0.75V and 0.8V; which is 6.25% of
reading difference. If required, the design could be calibrated to produce the same result as the commercial potentiostat.

Figure 5 voltammogram of 10mM ferricyanide from the designed potentiostat give the same shape with small difference in magnitude compared to the smooth curve output from the commercial potentiostat.

4. Conclusion

The development of 32-bit embedded algorithm using an ARM cortex processor with new developed potentiostat design for in-situ 3-electrode cell sensing were presented in this paper. By demonstrating that the device can produce the voltammogram of 10mM ferricyanide as expected, the capability of the developed device and its software algorithms to detect the redox reaction occur in chemical samples is possible. The device can generate an excitation signal of DPV from 0.4V to 1.2V and produced a peaked voltammogram with relatively small error compared to the commercial potentiostat. The design of potentiostat device and its DPV algorithm is verified.

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