

Design of Compact, Low-cost Electrochemical Electronic Reader (Potentiostat) for Chemical Compound Analysis

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Article Info

Article history:

Received Jul 28, 2025

Revised Dec 22, 2025

Accepted Dec 27, 2025

Keywords:

Biomedical instrumentation

Electronic reader

Low-cost

Electrochemical

Potentiostat

ABSTRACT

The development of low-cost electrochemical electronic reader (potentiostat) has been vastly growing recently since it could serve as a rapid chemical compound detection. Nevertheless, the realization of a low-cost potentiostat, having a compact size and providing multi-feature, is challenging. Here, a compact, low-cost potentiostat, supporting multi electrochemical methods was demonstrated. The total dimension was (10.8 x 4.6 x 3.5) cm³ with the weight of only 75.6 g. By using 16-bit analog-to-digital converter (ADC) and 12-bit digital-to-analog converter (DAC) components, the potentiostat facilitated a current input range of $\pm 580 \mu\text{A}$ with a resolution of 23.5 nA and a voltage sweep range of $\pm 1.5 \text{ V}$ with a resolution of 800 μV . For the electrochemical measurement, it supported cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods. Furthermore, in comparison with a commercial potentiostat (Sensit Smart), the potentiostat showcased a good accuracy performance. In detail, the average relative accuracy of the CV method test was 91% and 95% for the anodic (I_{anodic}) and cathodic peak currents (I_{cathodic}), respectively. For DPV method, the lowest relative accuracy of the peak current (I_{peak}) was still 83%. These results demonstrated that our potentiostat could promisingly be utilized for chemical compound detection in low-cost setting or rural areas.

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1. INTRODUCTION

Electrochemical measurements are widely utilized in various analytical biochemistry applications due to their excellent specificity, high sensitivity, fast analysis, and quantitatively measurable outputs [1], [2], [3], [4]. To name a few of their applications, include pathogen detection [5], biomarker detection and analysis [6], [7], concentration determination of a substance [8], and water contamination or quality analysis [9], [10]. Besides, the setup of an electrochemical measurement can be constructed using a low-cost system configuration without significantly compromising the performance. In detail, the electronics system, which performs the electrochemical measurements is named as potentiostat. When performing electrochemical measurements, potentiostat implements a particular electrochemical method. Which method to use for the measurement depends on what analyte or electrochemical reaction mechanism is going to be analyzed. The most common and basic methods to perform electrochemical measurement are the cyclic voltammetry (CV) and differential

pulse voltammetry (DPV). Basically, both methods are utilized to observe the redox reaction activities of the analytes, which highly correlate with their electrochemical reactions, concentration, and diffusion transport mechanism [11]. In particular, the DPV method applies a narrow step of voltage pulses – tens of millisecond, so that it produces a much more sensitive and selective signal outputs than the CV method [12].

Previous reports have demonstrated the design of low-cost potentiostats, built using Arduino-, Seeeduino- or ESP-based microcontroller boards. Arduino is the most widely explored low-cost microcontroller board due to its multi-purpose input-output (IO) pins, analog-to-digital converter (ADC), and digital-to-analog conversion features. Arduino-based low-cost potentiostats, which supported different multi electrochemical methods, such as cyclic voltammetry [13], chronoamperometry [14], [15], and linear sweep voltammetry [16], were demonstrated. Note that for Arduino boards with high specs, the board dimension is relatively wide. Hence, the only way for the integration with signal processing circuitry is typically via stacking configuration. Consequently, it is rather bulky due to its total height dimension. Seeeduino boards can be used as the alternative when higher specs are required. Low-cost potentiostats based on Seeeduino board capable of supporting multi electrochemical methods [17], heavy metal detection [18], and metabolite detection [19], were demonstrated. Note that the typical Seeeduino boards are about as wide as Arduino Uno. Thus, the system integration is also via stacking configuration. Meanwhile, the ESP boards have typically higher specs than Seeeduino boards and already come with integrated Bluetooth and Wi-Fi modules. More importantly, the ESP board dimension is typically as small as the Arduino Nano with the price is about similar to Arduino Uno. Therefore, a potentiostat built using ESP board would potentially not only have a high performance but also support wireless system operation and remote data monitoring [20], [21]. However, realizing a potentiostat, which is low-cost, compact, and supports multi electrochemical methods is still challenging due to the inherited limitations of the low-cost, general-purpose microcontrollers.

Therefore, the novel scientific contribution of this research is the demonstration of a compact and low-cost potentiostat, which supported multi electrochemical methods. It had a total dimension (including casing) of $\sim 174 \text{ cm}^3$ (10.8 cm x 4.6 cm x 3.5 cm). The low-cost ESP32 module was used as the microcontroller. Besides, to increase measurement data resolution, ADS1115 and MCP4725 were used as the 16-bit ADC and 12-bit DAC modules, respectively. Consequently, it could operate at a voltage sweep range of $\pm 1.5 \text{ V}$ with a fine resolution of $800 \mu\text{V}$ and an output current reading range of $\pm 580 \mu\text{A}$ with a resolution of as low as 23.5 nA . By having this high measurement data resolution, the potentiostat could support two electrochemical methods: CV and DPV. Furthermore, the scan rate variation and the multi-cycle test modes on the CV method could also be performed. More importantly, from the performance comparison with a commercial potentiostat, both CV and DPV measurements of the low-cost potentiostat exhibited a high accuracy with a relative accuracy of over 80% and a relative error of below 20%. These results demonstrated that our low-cost potentiostat (total cost: 25.44 USD) exhibited a high performance and supported multi-electrochemical methods, potentially applicable for the realization of rapid detection and analysis in remote areas, where access to health facilities is limited.

2. PROPOSED RESEARCH METHODS

2.1. Chemicals and Instrument

Potassium ferricyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]$) 99% was procured from Loba Chemie (Mumbai, India). P4417 phosphate buffered saline (PBS) tablet (Sigma Aldrich) was purchased from PT. Laborindo Sarana (Bandung, Indonesia). The screen-printed carbon electrode (SPCE) (Zimmer & Peacock HVSPE Carbon) was purchased from PT. Mitra Asiatek Biosensor. The commercial Sensit Smart potentiostat was purchased from PalmSens BV. All chemicals were used as received, unless otherwise indicated.

2.2. Potentiostat Schematic dan PCB Layout Design

The schematic and PCB layout design of the potentiostat are shown in Figure 1. The design consisted of several main circuits, which were buffer, summing amplifier, and transimpedance amplifier circuits. An additional Zener diode was also used as circuit protection to avoid any unwanted voltage spikes that could damage the ADC chip. In detail, the explanation of each main circuit block is elaborated in the following paragraphs.

1. Buffer

The buffer circuit is basically an amplifier with large output resistance, which can produce a high output current. Thus, this circuit is usually used to produce a sufficient signal amplification gain required for correct data processing or reading. In our potentiostat design, the buffer was placed after the DAC and before the ADC components since these two points were the crucial points, where the main signals passed through.

2. Summing Amplifier

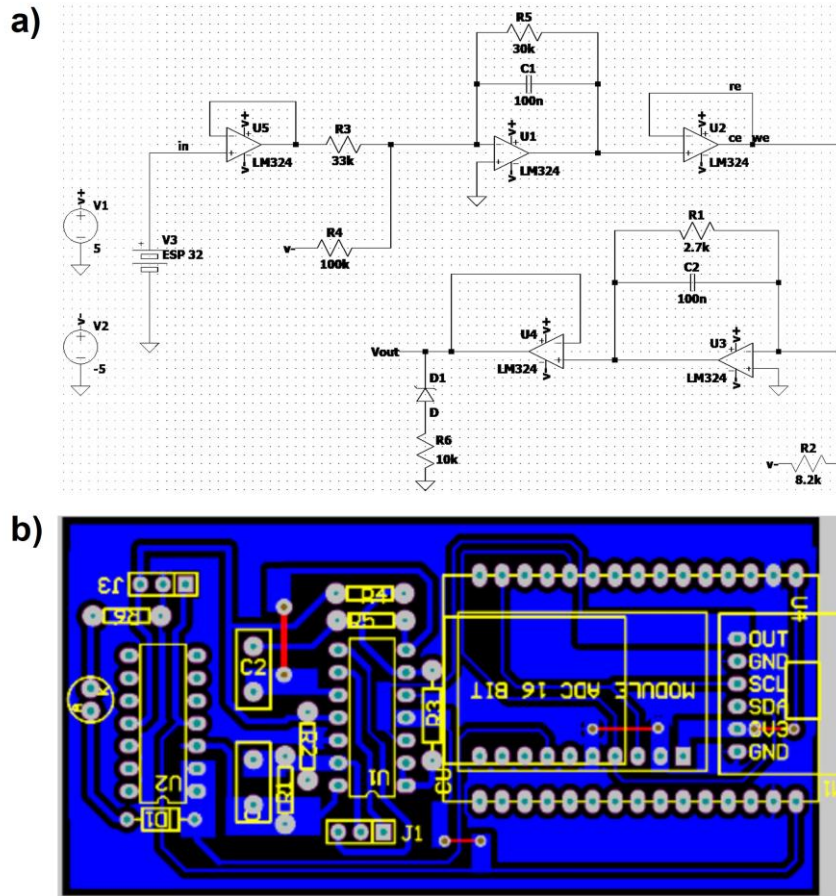


Figure 1. a) The schematic and b) PCB layout design of the potentiostat

The use of summing amplifier was to shift the working voltage range of the potentiostat. At first, the initial voltage range was 0 – 3.3 V, which was the ground voltage and the ESP32 module supply voltage, respectively. To facilitate electrochemical reactions, the voltage range must start from a negative voltage value. In our potentiostat design, the voltage range was shifted to -1.5 – 1.5 V (working voltage range). This working voltage range is considered wide enough to support many electrochemical biosensing applications, which include metabolite and aptamer detections [22], [23]. To produce this working voltage range, both positive and negative voltage supplies are required. In our design, LM2662 converter module was used to produce a negative -5 V. In detail, Equation 1-4 provides the calculation, including the required resistor values (in accordance with the schematic design in Figure 1a) to produce the desired working voltage range.

$$V_{\text{maximum range}} = -R_5 \times \left(\frac{V_{\text{ground}}}{R_3} - \frac{V_{\text{supply summing}}}{R_4} \right) \quad (1)$$

$$V_{\text{maximum range}} = -30000 \times \left(\frac{0}{33000} - \frac{5}{100000} \right) = 1.5V \quad (2)$$

$$V_{\text{minimum range}} = -R_5 \times \left(\frac{V_{\text{supply } \mu\text{controller}}}{R_3} - \frac{V_{\text{supply summing}}}{R_4} \right) \quad (3)$$

$$V_{\text{minimum range}} = -30000 \times \left(\frac{3.3}{33000} - \frac{5}{100000} \right) = -1.5V \quad (4)$$

Furthermore, to support a wide range of scan rate and to increase the data sampling resolution, an external 12-bit DAC module (MCP4725) was used. By using this module, the resolution of the DAC sweep voltage was ~730 μV , which was obtained from Equation 5. Note that due to the tolerance value of the resistors (Table 1) and the actual value of the negative voltage supply (-4.71 V), the actual DAC resolution was ~800 μV . This tolerance value would expectedly affect the measurement accuracy or error. Nonetheless, the tolerance value of an electrical component is unavoidable. Relative error of below 10% is already considered enough for low-cost DIY potentiostat [24].

$$Ideal\ resolution = \frac{1.5 - (-1.5)}{4096} = 0.732\ mV \quad (5)$$

Table 1. Ideal and actual resistors value used in the potentiostat circuit

Component name (Schematic Figure 1a)	Ideal resistor value (k Ω)	Actual resistor value (k Ω)
R ₃	33.0	32.6
R ₄	100.0	98.6
R ₅	30.0	32.5
R ₁	2.7	2.14
R ₂	8.2	8.01

3. Transimpedance Amplifier (TIA)

The transimpedance amplifier is the most important circuit block in the potentiostat as it converts the small current output signals, produced by the electrochemical sensor, into voltage signals, readable by the ADC module. In our design, the TIA circuit was based on inverting amplifier topology. Thus, the relationship between the output voltage of TIA (V_{out}) and the corresponding sensor output current (I_{WE}) can be calculated as in Equation 6 and Equation 7, respectively.

$$V_{OUT} = -R_1 \times \left(I_{WE} - \frac{V_{supply\ TIA}}{R_2} \right) \quad (6)$$

$$I_{WE} = \frac{V_{supply\ TIA}}{R_2} - \frac{V_{OUT}}{R_1} \quad (7)$$

In our design, the specification of the current input range was -600 – 600 μ A. Therefore, the possible resistors value for R₂ and R₁ were 8.2 k Ω and 2.7 k Ω , respectively. Note that due to the tolerance value of the resistors, the actual current range value was -580 – 580 μ A. Moreover, it is important to increase the resolution of the ADC since all the sensor data output was received by the ADC component. In our design, 16-bit ADS115 module was used as the external ADC component. By using this module, the measurement data resolution could be as small as ~23.5 nA.

2.3. Electrochemical Methods Parameters Setup and Analysis

1. CV Method

Generally, for CV method, there were four main input parameters:

- minimum applied voltage,
- maximum applied voltage,
- scan rate,
- number of cycles.

By our potentiostat circuit design, the minimum and maximum applied voltages were -1.5 V, and 1.5 V, respectively. In addition, when the diffusion phenomenon of the analyte towards the electrode is to be investigated, then the measurement with the variation of scan rate is required [25]. Meanwhile, the number of CV cycles could reflect the stability of the electrode for repeating measurements [26], [27]. Hence, to show the capability of our potentiostat to facilitate such measurements, scan rate variation and multi-cycle of CV measurements were conducted. In detail, the scan rate varied from 50, 70, and to 90 mV/s, while the multi-cycle CV test was performed for 5 cycles.

2. DPV Method

Meanwhile, for DPV method, the input signals had mainly five parameters to be set:

- minimum voltage,
- maximum voltage,
- step voltage,
- pulse voltage,
- pulse width.

Note that in the DPV method, in each single increment of the step voltage, the current was calculated twice. The first measured current was at the initial voltage, and the second measured current was at the voltage difference between the pulse voltage and the initial voltage. These two measured currents were then subtracted, and one point of the measured current value was obtained. Note that the current output resulted from the DPV method can mathematically be obtained from Equation 7.

To quantify the performance of the potentiostat, two metrics were used, which were relative error (Equation 8) and relative accuracy (Equation 9). Note that the ideal/reference current value was determined based on which reference measurement method was considered. In this research, it was either from the calculation of the Ohm's Law or from the measurement by a commercial potentiostat.

$$\text{Relative error} = \frac{|\text{current reading} - \text{ideal/reference current value}|}{\text{ideal/reference current value}} \times 100\% \quad (8)$$

$$\text{Relative accuracy} = \frac{\text{current reading by potentiostat}}{\text{reference current value}} \quad (9)$$

3. RESULTS AND DISCUSSION

3.1. Initial Tests Results using Resistor

The final dimension of the PCB design was $8.4 \times 4.2 \text{ cm}^2$, as shown in Figure 2a. With the addition of casing, the total dimension increased only slightly $10.8 \times 4.6 \times 3.5 \text{ cm}^3$ with a total mass of 75.57 grams. Initial tests using a resistor were then performed to confirm the basic functionality of the potentiostat. The resistor was connected between the working and the reference electrode to function as a constant load seen by the TIA circuit. The resistor value was then varied to confirm the linearity response of the potentiostat. For both CV and DPV methods, resistors with the following resistance values were used: 3.9 k Ω , 4.7 k Ω , 6.8 k Ω , 8.2 k Ω , and 10 k Ω . Afterwards, the current input of the TIA was measured by implementing the Ohm's Law to the voltage reading of the TIA input. The initial testing results of the CV method were shown in Figure 2b. Note that for this initial CV method test, the sweep voltage was set to $-0.5 - 0.5 \text{ V}$ as for the calculation easiness. From this test, the calculated R^2 values of the linear regression data from all the resistor variations were 0.999 (Table 2), which confirmed that the potentiostat exhibited a high linearity response.

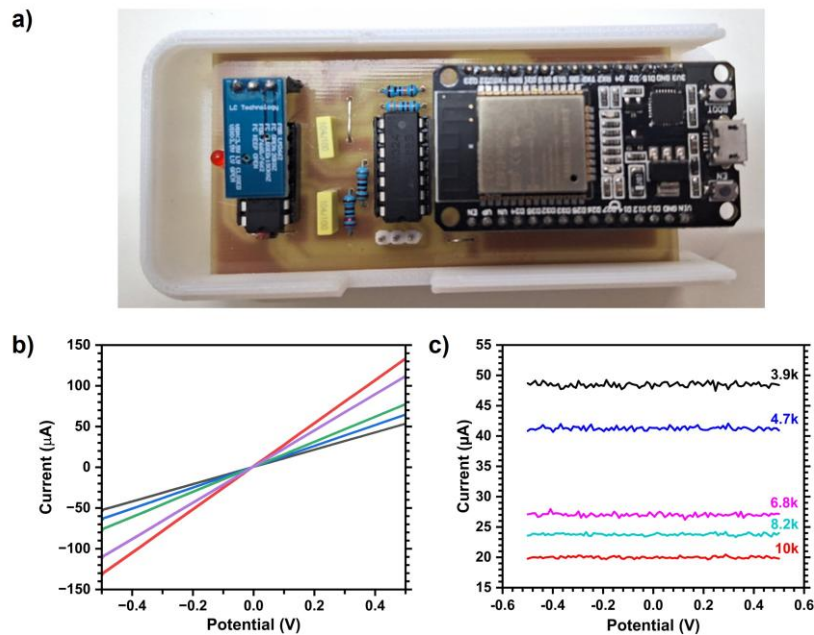


Figure 2. a) Photograph of the potentiostat including casing. b) CV and c) DPV test results toward different values of resistors

Table 2. Linearity and relative error of the CV method initial test using resistor

Resistor value (k Ω)	CV method R^2	DPV method Relative error (%)
3.9	0.99988	5.4
4.7	0.99988	3.9
6.8	0.99986	3.1
8.2	0.99987	2.0
10	0.99983	1.0

Similarly, the initial test procedures were performed using DPV method. For the DPV method, the resulting current response was calculated from the voltage output divided by the value of the resistor being used. The initial testing results of the DPV method were shown in Figure 2c. Moreover, the relative error of the DPV method test was also calculated. In this DPV method test, the ideal and the current reading were all obtained by applying a voltage supply of 0.2 V, which was the DPV pulse voltage. Additionally, the ideal current was calculated by the Ohm's Law. The results (Table 2) show that the relative errors of the DPV method test were all below 6%, which means that the potentiostat showcased a good measurement accuracy performance.

3.1. Experimental Tests using Chemical Compound (Potassium Ferricyanide Electrolyte)

By using the same test procedures as the initial CV method test, the experimental CV method test using a chemical compound (potassium ferricyanide electrolyte) was performed. It is common to use potassium ferricyanide electrolyte to evaluate the cyclic voltammetry signal response due to its reversible redox reaction, producing observable and distinctive oxidation and reduction peaks [28], [29], [30]. For the test of concentration variation, the scan rate was set to 100 mV/s and the electrolyte concentration was varied from 5, 10, and to 20 mM. The results were shown in Figure 3a. It can be seen that by increasing the concentration of the electrolyte, both oxidation and reduction peak currents increased and decreased, respectively. The change of these peak currents was due to the change in the number of ions presented in the electrolyte solution. In the case of ionic or electrolytic analyte, the higher the concentration was, the higher the electrical charge would be [31], [32]. Therefore, these results confirmed that the potentiostat could correctly read the sensor output current when the analyte/electrolyte concentration was changed.

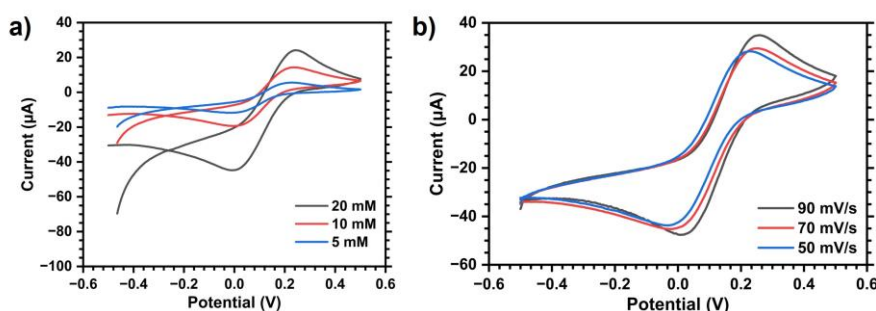


Figure 3. CV method test results toward the variation of the a) electrolyte concentration and the b) scan rate

Moreover, the scan rate variation experiment was also conducted. The scan rate was varied from 50, 70, and to 90 mV/s. By the phenomenon of ions diffusion onto the electrode, the slower the scan rate, the thicker the diffusion layer would be [33], [34]. Hence, it would inhibit the electron transfer, which resulted in smaller output current response. The results, shown in Figure 3b, well agreed with the phenomenon, which indicated that the potentiostat could correctly read the current output when the scan rate was varied.

Additionally, a multi-cycle CV method test was also performed. The test was conducted for 4 consecutive cycles. The potentiostat could successfully apply the multi-cycle test. As shown in Figure 4, both the anodic and cathodic peak currents deviated only very slightly. In detail, the standard deviation of the 4-cycle oxidation and reduction peaks were 1.23 and 0.33, respectively. The slight variation of these current outputs was common and resulted from the variation of the electrochemical reaction variation or the electrode reactivity itself [35], [36]. Hence, this result showed that our potentiostat successfully performed multi-cycle CV method and correctly read the current output of the sensor.

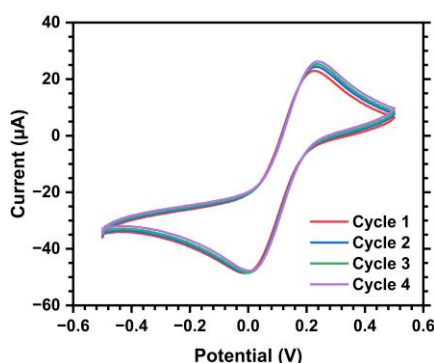


Figure 4. CV method test results for over 4 consecutive cycles.

3.3. Performance Comparison with Commercial Potentiostat

The accuracy of the potentiostat was evaluated by comparing the current output peaks of both CV and DPV methods with the commercial Sensit Smart potentiostat. Table 3 shows the comparison of the 4-cycle CV method current output peaks (I_{anodic} and I_{cathodic}). From the test results, even for the 4 consecutive cycles of measurement, the relative accuracy of the current output was all above 85%, while the relative errors were all below 15%. These results showcased that the potentiostat exhibited good reproducibility for CV method measurements in comparison with the commercial potentiostat. Additionally, the comparison test was also conducted for the DPV method. The results, provided in Table 4, show that the potentiostat exhibited good accuracy for DPV method test as well. The relative accuracy of the DPV peak current (I_{peak}) and voltage (V_{peak}) were all above 80% and the corresponding relative errors were all below 20%. The relative error of the V_{peak} could further be improved by utilizing DAC component with higher resolution specification.

Table 3. Relative accuracy and error comparison of the 4-cycle CV method test

Current Peak	Cycle				Average
	1	2	3	4	
Potentiostat (this work)					
I_{anodic} (μA)	39.8	41.5	41.4	43.4	39.6
I_{cathodic} (μA)	-39.4	-38.6	-38.4	-38.6	-38.9
Sensit Smart					
I_{anodic} (μA)	44.4	43.7	47.4	48.3	43.5
I_{cathodic} (μA)	-41.2	-38.2	-39.4	-39.7	-40.8
Relative Accuracy					
I_{anodic} (%)	89.6	94.0	87.2	89.8	91.1
I_{cathodic} (%)	95.6	99.1	97.5	97.1	95.0
Relative Error					
I_{anodic} (%)	10.4	5.0	12.7	10.2	8.9
I_{cathodic} (%)	4.4	0.9	2.5	2.9	4.0

Table 4. Relative accuracy and error comparison of the DPV method test

Concentration (mM)	5	10	20
Potentiostat (this work)			
I_{peak} (μA)	22.23	36.29	58.56
V_{peak} (V)	0.09	0.10	0.14
Sensit Smart			
I_{peak} (μA)	20.93	34.89	50.05
V_{peak} (V)	0.10	0.12	0.14
Relative accuracy			
I_{peak} (%)	93.78	95.98	82.99
V_{peak} (%)	87.38	81.30	97.90
Relative error			
I_{peak} (%)	6.22	4.02	17.01
V_{peak} (%)	12.62	18.70	2.10

Table 5. Performance comparison of the low-cost potentiostats

Methods (measurement mode)	Voltage range (V)	Current range (μA)	ADC resolution bit and (μA)	DAC resolution bit and (μV)	Price (USD)	Ref.
CV, LSV, CA (scan rate variation)	± 1.5	± 225	10	8	25	[16]
CV	± 1.5	± 300	12 (0.16)	8 (11700)	25.12	[21]
CV, CA, ASV	± 2.5	± 500	10	8 (19500)	40	[13]
CV, CA (scan rate variation)	± 3.3	± 13750	16 (1)	12 (1600)	45.76	[14]
CV, LSV, DPV, CA	± 1.65	± 150	12	10 (3300)	15	[18]
CV, LSV, DPV, SWV, NPV, CA (scan rate variation)	± 1.5	± 500	12	12 (800)	21.4	[37]
CV, DPV (scan rate variation, multi cycles)	± 1.5	± 580	16 (0.0235)	12 (800)	25.44	This work

CV = cyclic voltammetry, DPV = differential pulse voltammetry, LSV = Linear Sweep Voltammetry, CA = chronoamperometry, ASV = anodic stripping voltammetry, SWV = square wave voltammetry, NPV = normal pulse voltammetry

From the comparison test results of both CV and DPV methods, a margin of the current output as well as the V_{peak} could be clearly observed. One possible reason causing this margin was the slight conductivity variation of the SPCE itself, which could be originated from the dimension variation of the electrodes during batch production. Additional physical or chemical surface treatments could be useful to minimize these variations [38]. Further analysis on the performance margin could also be obtained by conducting electrochemical impedance spectroscopy (EIS) measurement. In EIS measurement, the electrokinetics of the charges at the electrolyte and the electrode could be estimated and thus providing in-depth insights on the overall electrochemical cell system [39]. Nonetheless, in overall, the potentiostat could still produce current output peaks, which were relatively comparable with the commercial product. Thus, our potentiostat could firmly serve as the low-cost alternative for electrochemical measurements involving CV and/or DPV method test. Moreover, though the potentiostat is currently supporting two electrochemical methods (CV and DPV), other methods or techniques (amperometric and potentiometric) can actually be implemented by further additional code programming of the ESP32 microcontroller. Nevertheless, the measurement limitation would be the implementation of impedimetric techniques. The impedimetric techniques require higher specification of an analog front end chip such as AD5941 chip. The chip supports high bandwidth current signals (200 kHz) and includes a discrete Fourier Transform engine, which essential to compute the real and imaginary part of the impedance signal [40], [41].

Furthermore, performance comparison with the previously reported low-cost potentiostats was provided in Table 5. Based on this comparison, it can be concluded that our potentiostat was low-cost, but supported a fine resolution for both current input and sweep voltage. Besides, although the supported electrochemical method was still limited. However, the potentiostat also supported scan rate variation and multi cycles measurement mode. Thereby, our potentiostat presented as a competitive solution for providing low-cost basic electrochemical measurement applications.

4. CONCLUSION

This study aims to develop a compact, low-cost potentiostat, which supports multi-electrochemical methods. The results showcased a potentiostat with a compact design with a total dimension of (10.8 x 4.6 x 3.5) cm³ and a mass of only 76.6 g. By utilizing external ADC and DAC components, the potentiostat had a voltage sweep range of ± 1.5 V with 800 μ V voltage resolution and a current input range of ± 580 μ A with current resolution of 23.5 nA. Furthermore, the potentiostat supported both CV and DPV methods with the overall relative accuracy of more than 80% and relative error of below 20% in comparison with the commercial potentiostat. For further improvement, additional firmware programs could also be added to the microcontroller to support other electrochemical methods, such as amperometry and electrical impedance spectroscopy. By these continuous improvements on the low-cost potentiostats, we anticipate that in the future, the potentiostat could promisingly be utilized as an early screening platform for health diagnostics in remote areas.

ACKNOWLEDGMENTS

This research received partial funding from Telkom University through the 2025 Non-external Research Collaboration Scheme (1st Period, 1st Call) with grant number 248/LIT06/PPM-LIT/2025.

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