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SweepStat: A Build-It-Yourself, Two-Electrode Potentiostat for Macroelectrode and Ultramicroelectrode Studies

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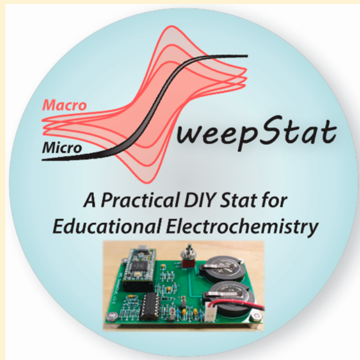
Supporting Information

ABSTRACT: Experimental electrochemistry offers unique opportunities for interactive instruction at all levels of education; however, widespread adoption in curricula is hindered by high costs associated with electrochemical instrumentation. Thus, the development of affordable instruments represents an essential step toward making electrochemistry accessible to everyone. While numerous commercially available three-electrode potentiostats exist, two-electrode potentiostats provide a simple and inexpensive alternative. Herein, we present the two-electrode SweepStat as a low-cost option capable of performing voltammetry and amperometry with comparable data acquisition to commercially available potentiostats valued from $4,000−40,000 USD. Additionally, the SweepStat's design facilitates current measurements in the nanoampere regime, permitting experiments with ultramicroelectrodes (UMEs; $r_{electrode}$ < 25 μm). The fabrication, programming, and testing of this device constitute a valuable experimental exercise at the intersection of circuit design and construction, computer programing, and electrochemical analysis. A set of simple electrochemical experiments are presented for both macroelectrodes and UMEs, highlighting key electrochemical techniques, equations, and concepts. Furthermore, finite element modeling and commercial potentiostat comparisons are used to verify the efficacy of the SweepStat platform. The open-source nature of the SweepStat coupled with the wealth of electrochemical techniques and experiments that can be implemented with a simple two-electrode circuit offers an unparalleled opportunity for electrochemical instruction with extensive method development driven by student research.



KEYWORDS: *Electrochemistry, Instrumental Methods, Undergraduate Research, Analytical Chemistry, Hands-On Learning/Manipulatives*

■ INTRODUCTION

A number of low-cost electrochemical instrumentation suites have been developed[1−6] to offer accessible instrumentation for electrochemical measurements in educational settings, among which the most cited are the DStat from Wheeler,[7] the Cheapstat from Plaxco,[8] and the RodeoStat from IORodeo. These potentiostats use inexpensive mass-produced printed circuit boards coupled with Arduino microprocessors or comparable microcontrollers to interface with personal computers for electrochemical measurements. A comparison of key properties for three low-cost potentiostats is presented in Table 1.

With all of these low-cost potentiostats, classical CV measurements, which are detailed in the Supporting Information, can be conducted using a macrodisk electrode to provide voltammograms similar to Figure S1 at a fraction of the cost compared to commercial potentiostats. However, all three options employ a three-electrode cell, including a SHE, SCE, or Ag/AgCl reference electrode (RE), thereby complicating the circuitry required for the measurement and increasing the learning curve for student assembly. Additionally, the current ranges for these instruments have limits (i.e., ±1 μA for the Rodeostat) that are insufficient to characterize electrochemical processes at ultramicroelectrodes (UMEs) or nanoelectrodes without further signal gain modification. The DStat was the first of these devices to allow chronoamperometric measurements, where the current is measured at a constant potential. Recently, development has switched to more user-friendly Arduino microcontrollers from integrated microprocessors, appealing to the ease-of-use requirements for undergraduate or secondary education instruction. Because UMEs are becoming commonplace in the field,[9−11] there is a need to integrate macroelectrode and UME sensitivities on the same instrument. The counter electrode (CE) component of the three-electrode system may be removed since small currents (<10 nA) are passed at an UME, resulting in a two-

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Table 1. Key Instrumentation Parameters for Previously Reported Low-Cost Potentiostats

	Cheapstat	DStat	Rodeostat	SweepStat (This Work)
Year released	2011	2015	2017	2019
Price[a] (USD)	$80	$120	$250	$55
Assembly	Assembled	Unassembled	Assembled	Unassembled
Computer interfacing	USB	USB	USB	USB
Microcontroller	Amtel XMEGA	ATxmega256A3U	Arduino Teensy 3.2	Arduino Teensy 3.2
Electrodes	Three	Three	Three	Two
GUI	Built in	Python	Python	LabView
Potential range	−0.8 to 1.6 V	3.3 V window	±1, 2, 5, 10 V	−1.5 to 1.5 V
Current range (μA)	±10, 50	Unreported	±1, 10, 100, 1000	±0.015, 1.5
IO resolution	2400 In, 3300 Out	16 bit In, 16 bit Out	12 bit In, 13 bit Out	16 bit In, 12 bit Out
Experimental capabilities	Voltammetry (CV), Voltammetry (LSV)	Voltammetry (CV), Chronoamperometry	Voltammetry (CV), Voltammetry (LSV), Chronoamperometry, Step voltammetry, AC voltammetry	Voltammetry (CV), Voltammetry (LSV), Chronoamperometry, Chronocoulometry

[a]Prices indicated based on initial literature reports and are subject to change.

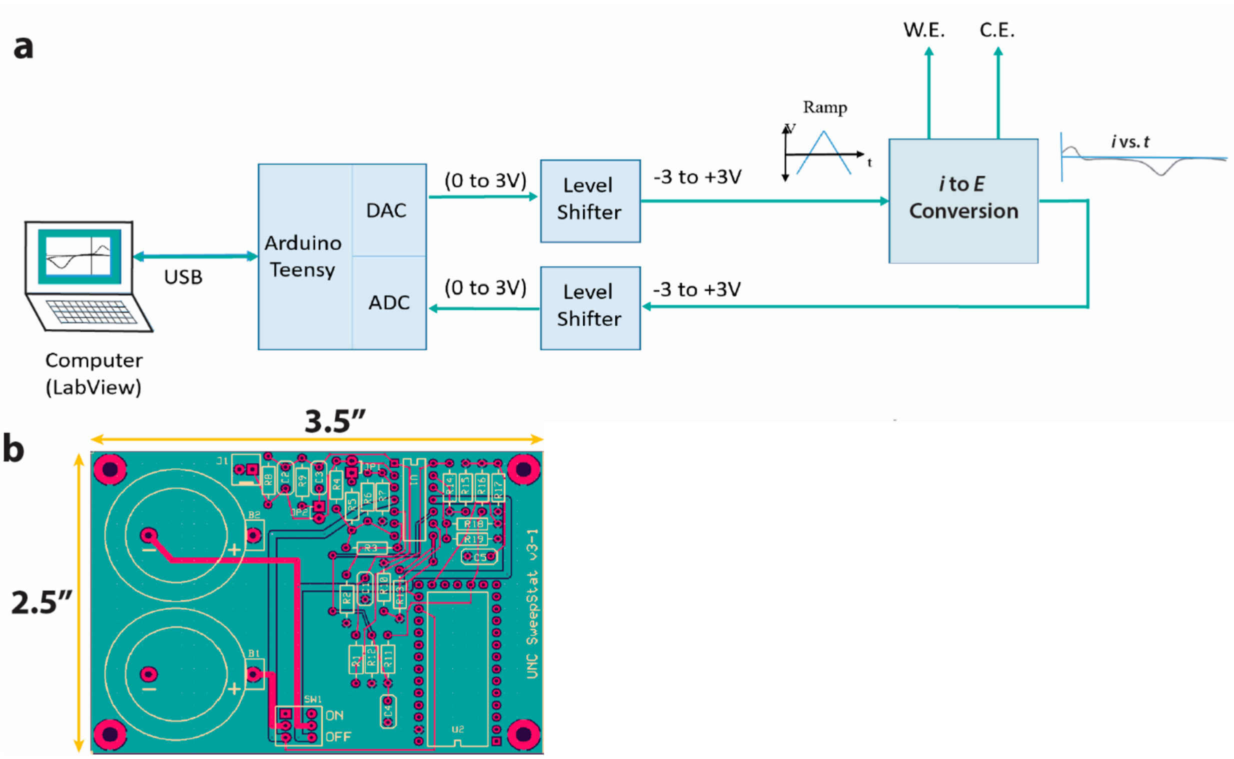

Figure 1. (a) Block diagram of SweepStat circuitry demonstrating Arduino Teensy 3.2 interface with LabView GUI, voltage shifting for a total potential range of 3 V, current−potential amplifiers for both macrodisk and UME electrochemistry, and reverse-level shifting. (b) Printed circuit board (PCB) generated for SweepStat device. Details for SweepStat construction, including a comprehensive part list and circuit diagram, can be found in the Supporting Information.

electrode system where one electrode acts as both the CE and RE. Several benefits result from this configuration, including simplified circuitry, straightforward electrode preparation, and access to high-frequency measurements such as FSCV (Figure S2).

Herein, we present the SweepStat, a low-cost open-source potentiostat that can conduct cyclic voltammetry and chronoamperometry at both macrodisk electrodes and UMEs with a total fabrication cost of $55 USD (cost breakdown is detailed in the Supporting Information). The SweepStat employs a two-electrode cell with a combined reference/counter electrode to reduce circuit complexity and fabrication cost while opening the possibility for future high-frequency integration. By integrating simple jumper switches into the circuit design, two gain modes (1 μA/V and 10 nA/V) were established for macroelectrode and UME experimentation. This design employs an Arduino Teensy 3.2 microcontroller with an open-source LabView executable and intuitive graphical user interface (GUI) for informative real-time data visualization. By combining macrodisk and UME capabilities with voltammetry and chronoamperometry, the SweepStat offers a wide range of electrochemical measurement capabilities compared to other low-cost potentiostats at the lowest overall price point, opening the possibility to implement a comprehensive survey of electrochemistry into undergraduate or secondary education chemistry curricula with engaging, practical, and research-oriented experimentation. Devices were constructed and tested by graduate and

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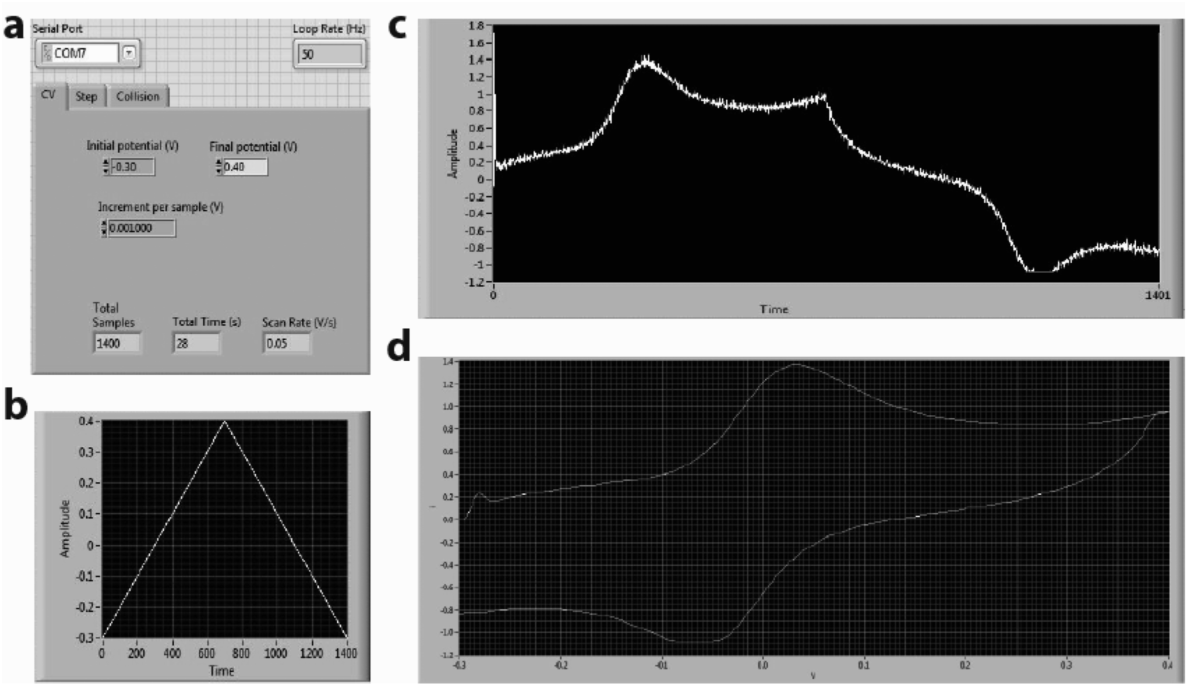

Figure 2. (a) LabView GUI for cyclic voltammetry showing variable experimental parameters. (b) Voltage ramp generated to drive reactions at electrode interface. (c) Raw current output before low-pass filtering and voltage fitting to generate colloquial CV shape. (d) Final voltammogram at a gain setting of 1 μA/V plotted in IUPAC convention by default. Conversion to classical convention was manually applied for data processing.

undergraduate students in the electroanalytical chemistry course (CHEM 445) at the University of North Carolina at Chapel Hill in Fall 2018. Furthermore, the efficacy of the device is validated using commercially available potentiostats (CH Instruments 601E) and finite-element modeling software (COMSOL Multiphysics), constituting a comprehensive exercise in electrochemical analysis and simulation.

UNDERSTANDING THE SWEEPSTAT DEVICE AND USER INTERFACE

The block-diagram and printed circuit board (PCB) design for the SweepStat are presented in Figure 1. An Arduino Teensy microprocessor was chosen to convert the signal from the two-electrode system and transfer it to the host computer via USB for analysis and plotting due to its small size, chip-like form factor, and low price. Unfortunately, the Arduino series of microprocessor boards are built using a single 5 V DC power source which forces the digital-to-analog converter (DAC) and analog-to-digital converter (ADC) to be unipolar instead of bipolar. The signals to and from potentiostats must be bipolar in order to accommodate negative ramp voltages and outputs. This was accomplished by using two coin cells in series with the common tied to ground. However, additional circuitry was included to level shift signals from the Arduino Teensy DAC and into the ADC (Figure 1a). The simplified block diagram outlines the user selection of a voltage signal to be applied to the cell from the LabView GUI and subsequent conversion to an actual potential to be applied to the WE via the DAC (Figure 1a). Furthermore, the voltage signal proportional to the current in the cell is routed to the Arduino's ADC and subsequently plotted in the LabView GUI. Because the Arduino Teensy is limited to an input−output voltage (IO) of 0 to +3 V, level-shifting is required to generate negative voltages. The measured current is subsequently fed back through a level-shifter to produce positive voltages that the Arduino can process prior to LabView analysis. This design strategy facilitates the use of various waveforms generated by the LabView interface to perform voltammetric and amperometric experiments. For instance, a constant DC waveform may be applied to make chronoamperometric measurements. The PCB design was created with Express PCB Layout software and fabricated off-site by Express PCB (Figure 1b). A detailed circuit diagram for the SweepStat, as well as a comprehensive materials list, can be found in the Figure S6 and Table S1. SweepStat assembly was completed in approximately 2 h with conventional component hand-soldering and does not require advanced soldering experience or techniques to construct. We further present a step-by-step procedure on the SweepStat assembly in the Supporting Information. The device was housed in a custom 3D-printed enclosure to protect the electronic components (Figure S3). Operation of the SweepStat was facilitated by the open-source LabView executable included in the supporting documents and discussed in detail in the Supporting Information. The executable is also available free-of-charge at nanoelectrochemistry.com and will be updated regularly with new techniques and support.

SWEEPSTAT OPERATION

Electrochemical characterization of the SweepStat was conducted at both the macroelectrode (μA) and UME (nA) scale using cyclic voltammetry and amperometry. Macrodisk characterization was achieved by taking CVs of a 75 μM ferrocenemethanol aqueous solution with 100 mM potassium chloride supporting electrolyte on a glassy carbon macrodisk electrode and cycling the potential from −0.3 to +0.4 V at three scan rates (50, 25, and 12.5 mV/s). Subsequently, the amperometric function of the SweepStat was tested in 75 μM ferrocenemethanol with 250 mM potassium chloride using single-step chronoamperometry. The potential was held at 0 V

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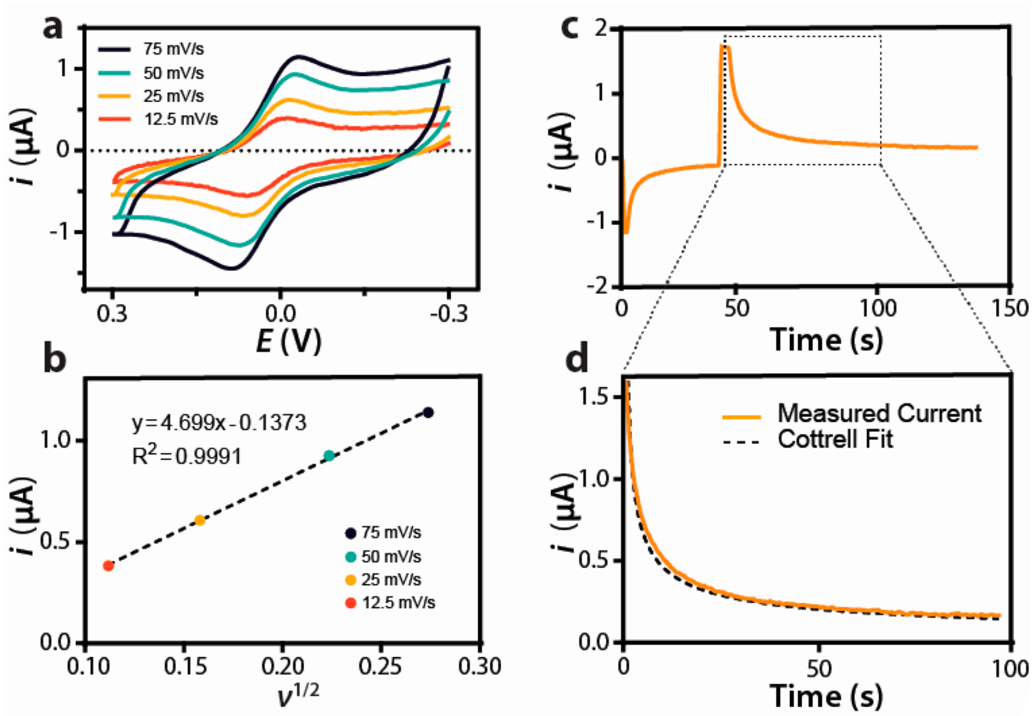

Figure 3. (a) Cyclic voltammograms of 75 μM ferrocenemethanol oxidation on a 1.5 mm glassy carbon macrodisk electrode. (b) Oxidative peak current plotted as a function of the square root of scan rate, elucidating the linear relationship with $\nu^{1/2}$ as outlined by the Randles–Sevcik equation. (c) Current–time trace of bulk electrolysis of ferrocenemethanol following a potential step from 0 to 0.4 V. (d) Polynomial fit following $t^{-1/2}$ as outlined by the Cottrell equation. SweepStat gain was 1 μA/V for all experiments.

for 5 s followed by a potential step to 0.6 V for 25 s, an anodic overpotential sufficient to oxidize ferrocenemethanol. Additionally, cyclic voltammetry was performed at a Pt UME in a 7.5 mM potassium ferrocyanide solution with 250 mM potassium chloride by sweeping the working potential from −0.3 to +0.4 V at a scan rate of 50 mV/s. Figure 2a shows the LabView GUI used to input these parameters. Panels b and c of Figure 2 show the voltage ramp generated at the WE interface and the raw current response obtained as a function of time, respectively. Figure 2d shows the filtered, voltage-corrected voltammogram as a final output. A step-by-step experimental procedure for SweepStat construction and electrochemical testing is provided in the Supporting Information. The microscopic working electrode area of an UME necessitates the use of a Faraday cage to eliminate noise related to electromagnetic (EM) radiation. Such cages are simple to construct by wrapping a grounded conductive metal sheet, such as aluminum foil, around the electrochemical cell. For convenience, a detailed procedure regarding the construction of a functional Faraday cage is included in Figure S8.

■ ELECTROCHEMICAL EXPERIMENTATION USING THE SWEEPSTAT

An extensive introduction to electrochemical measurements at macro- and ultramicroelectrodes can be found in the Supporting Information, with specific attention given to mass transfer effects on the shape of the voltammogram (Figure S4). For the experiments outlined in SweepStat Operation, the reversible oxidation of 75 μM ferrocenemethanol on a 1.5 mm radius glassy carbon electrode was studied at varying scan rates using the SweepStat. For a Nernstian, one-electron transfer process occurring on a macrodisk electrode, the peak oxidative or reductive current is governed by the Randles–Sevcik equation:

$$i_p = 268{,}600 n^{3/2} C^* A D^{1/2} \nu^{1/2} \quad (1)$$

where n is the number of electrons, C^* is the bulk concentration of the analyte, D is the diffusion coefficient of the analyte, A is the electrode area, and ν is the scan rate. By varying the CV scan rate in a solution of known concentration, number of electrons transferred per molecule, and electrode area, the diffusion coefficient for a given species can be extracted. Within the SweepStat GUI, the scan rate for a CV sweep can be controlled by modifying the potential increment. Successive CV scans for the oxidation of ferrocenemethanol are presented in Figure 3a with an associated plot of the peak current as a function of the square root of scan rate in Figure 3b, which is linear, as predicted by the Randles–Sevcik equation. The nonzero y-intercept in Figure 3b corresponds to the non-faradaic, capacitive current. From the slope of a linear least-squares regression fit extracted from Figure 3b, the diffusion coefficient for ferrocenemethanol can be calculated at a value of 11 × 10^{-6} cm^2/s.[12]

Beyond voltammetry, chronoamperometry can be studied using the SweepStat as outlined in Electrochemical Experimentation Using the SweepStat. Amperometric i–t traces can be used to extract several electrochemical properties on the basis of the current decay following a potential step to a sufficiently cathodic potential. This behavior is described by the Cottrell equation:

$$i(t) = nFAD^{1/2} C^* \pi^{-1/2} t^{-1/2} \quad (2)$$

where F is Faraday's constant and n, A, D, C^*, and t are as previously defined. By setting $t = 0$ at the start of current decay,

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a current−time transient can be fitted as presented in Figure 3c,d. From this plot, a polynomial fit following $t^{-1/2}$ can be calculated to provide a diffusion coefficient value of 15×10^{-6} cm^2/s, showing good agreement with the CV derived value.

Similar to cyclic voltammetry at a macrodisk electrode, current−potential measurements can be conducted on UMEs with diameters less than 25 μm (about half the diameter of a human hair) to provide electrochemical and physical properties. Of note, given the small electroactive surface area of an UME, a steady-state current is reached at the electrode surface nearly instantaneously upon reaching the oxidation potential with a current controlled by radial diffusion of analyte to the inlaid disk electrode surface given by

$$i_{ss} = 4nFC^{*}Dr_{\mathrm{UME}} \tag{3}$$

where n, F, D, and C^* are as previously defined, and r_{UME} is the radius of the UME. This equation is only valid for UMEs of a specific geometry (inlaid disk, $r_{\mathrm{insulator}} > 10r_{\mathrm{UME}}$) but can be separately derived for different geometries.[13] For redox processes at the surface of an UME under radial diffusion control, the concentration gradient does not change with time. For a 7.5 mM solution of potassium ferrocyanide, the steady-state voltammogram at a UME is presented in Figure 4 with a

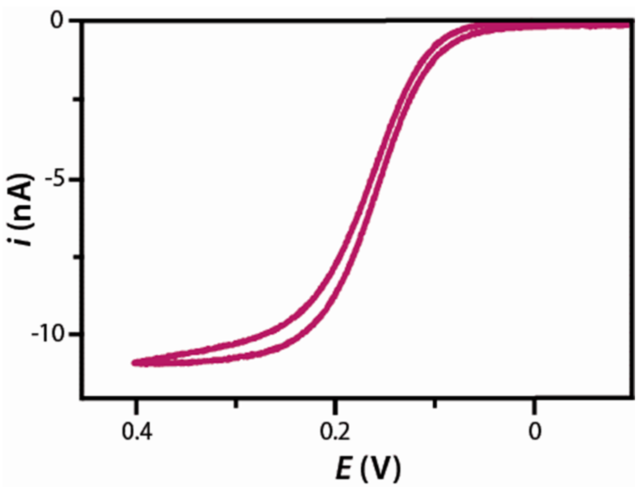

Figure 4. Voltammogram of 7.5 mM potassium ferrocyanide solution oxidized at a 5 μm radius platinum UME with a steady state current of ~11 nA. SweepStat gain at 10 nA/V and scan rate of 50 mv/s.

calculated diffusion coefficient value of 7.60×10^{-6} cm^2/s.[14] Both macro- and ultramicroelectrode voltammograms were validated using a commercial potentiostat as well as COMSOL Multiphysics, a finite-element simulation software (Figure S5). Various parameters used for simulations are included in the Supporting Information to enhance the educational value this work.

CONCLUSION

SweepStat is presented as a low-cost, open-source, instructional electrochemical workstation that allows for measurements comparable to commercially available high-end potentiostats at a significantly reduced cost. By using a two-electrode electrochemical cell, the SweepStat can be fabricated with minimal technical experience in approximately 2 h for under $55 USD. Cyclic voltammetry and amperometry measurements at macrodisk electrodes and UMEs offer high-quality data that corresponds to literature reported values, commercially available electrochemical workstations, and finite-element simulation packages. By employing an open-source hardware, GUI, and enclosure design, SweepStat offers modularity and ease of integration into conventional chemistry curricula at the undergraduate and secondary education levels. While additional electrochemical method modules can feasibly expand the functionality of SweepStat, the wide range of electrochemical experiments and phenomena that can be explored through simple voltammetry and amperometry is evident on the basis of previous reports regarding electrochemistry as an instructional tool. Overall, SweepStat can be used as a tool to augment conventional chemistry courses with tangible and practical experimental data that are accessible and engaging for students while offering extensive opportunities for student-driven ingenuity and innovation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at https://pubs.acs.org/doi/10.1021/acs.jchemed.9b00893.

Introduction to electrochemistry, detailed discussion of two and three electrode systems, 3D-printed enclosure design method, list of materials for diffusion coefficient experiments, overview of macro- and microelectrode chemistry, comparison of SweepStat to commercial instrumentation and theoretical simulations, circuit and PCB diagrams, SweepStat assembly and testing procedure, COMSOL modeling procedure and parameters, and a complete list of SweepStat components (PDF; DOCX)

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Notes

The authors declare no competing financial interest.
Executable Software for SweepStat 1.0 is available online at www.nanoelectrochemistry.com → SweepStat Page.

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REFERENCES

(1) Meloni, G. N. Building a Microcontroller Based Potentiostat: A Inexpensive and Versatile Platform for Teaching Electrochemistry and Instrumentation. *J. Chem. Educ.* **2016**, *93* (7), 1320−1322.

(2) Lopin, P.; Lopin, K. V. PSoC-Stat: A single chip open source potentiostat based on a Programmable System on a Chip. *PLoS One* **2018**, *13* (7), No. e0201353.

DOI: 10.1021/acs.jchemed.9b00893
J. Chem. Educ. XXXX, XXX, XXX−XXX

(3) Bezuidenhout, P.; Smith, S.; Joubert, T.-H. A Low-Cost Inkjet-Printed Paper-Based Potentiostat. *Appl. Sci.* **2018**, *8* (6), 968.
(4) Li, Y. C.; Melenbrink, E. L.; Cordonier, G. J.; Boggs, C.; Khan, A.; Isaac, M. K.; Nkhonjera, L. K.; Bahati, D.; Billinge, S. J.; Haile, S. M.; Kreuter, R. A.; Crable, R. M.; Mallouk, T. E. An Easily Fabricated Low-Cost Potentiostat Coupled with User-Friendly Software for Introducing Students to Electrochemical Reactions and Electroanalytical Techniques. *J. Chem. Educ.* **2018**, *95* (9), 1658−1661.
(5) Meloni, G. N. 3D Printed and Microcontrolled: The One Hundred Dollars Scanning Electrochemical Microscope. *Anal. Chem.* **2017**, *89* (17), 8643−8649.
(6) Ainla, A.; Mousavi, M. P. S.; Tsaloglou, M.-N.; Redston, J.; Bell, J. G.; Fernández-Abedul, M. T.; Whitesides, G. M. Open-Source Potentiostat for Wireless Electrochemical Detection with Smartphones. *Anal. Chem.* **2018**, *90* (10), 6240−6246.
(7) Dryden, M. D. M.; Wheeler, A. R. DStat: A Versatile, Open-Source Potentiostat for Electroanalysis and Integration. *PLoS One* **2015**, *10* (10), No. e0140349.
(8) Rowe, A. A.; Bonham, A. J.; White, R. J.; Zimmer, M. P.; Yadgar, R. J.; Hobza, T. M.; Honea, J. W.; Ben-Yaacov, I.; Plaxco, K. W. Cheap Stat: An Open-Source, "Do-It-Yourself" Potentiostat for Analytical and Educational Applications. *PLoS One* **2011**, *6* (9), No. e23783.
(9) Glasscott, M. W.; Dick, J. E. Direct Electrochemical Observation of Single Platinum Cluster Electrocatalysis on Ultramicroelectrodes. *Anal. Chem.* **2018**, *90* (13), 7804−7808.
(10) Peng, Y.-Y.; Qian, R.-C.; Hafez, M. E.; Long, Y.-T. Stochastic Collision Nanoelectrochemistry: A Review of Recent Developments. *ChemElectroChem* **2017**, *4* (5), 977−985.
(11) Dick, J. E.; Renault, C.; Bard, A. J. Observation of Single-Protein and DNA Macromolecule Collisions on Ultramicroelectrodes. *J. Am. Chem. Soc.* **2015**, *137* (26), 8376−8379.
(12) Cannes, C.; Kanoufi, F.; Bard, A. J. Cyclic voltammetry and scanning electrochemical microscopy of ferrocenemethanol at monolayer and bilayer-modified gold electrodes. *J. Electroanal. Chem.* **2003**, *547* (1), 83−91.
(13) Zoski, C. G.; Mirkin, M. V. Steady-State Limiting Currents at Finite Conical Microelectrodes. *Anal. Chem.* **2002**, *74* (9), 1986−1992.
(14) Barker, A. L.; Unwin, P. R. Measurement of Solute Partitioning across Liquid/Liquid Interfaces Using Scanning Electrochemical Microscopy-Double Potential Step Chronoamperometry (SECM-DPSC): Principles, Theory, and Application to Ferrocenium Ion Transfer Across the 1,2-Dichloroethane/Aqueous Interface. *J. Phys. Chem. B* **2001**, *105* (48), 12019−12031.

DOI: 10.1021/acs.jchemed.9b00893
J. Chem. Educ. XXXX, XXX, XXX−XXX