PSOC BASED POTENTIOSTAT

Mr.Nikhil Amala Jerrin J[#1] , Mr. Jaieswar S[*2], Mr. Harish A[^3]

[#] *Student, Department of Mechatronics, Bannari Amman Institute Of technology, Erode,India*

[*] *Student, Department of Mechatronics, Bannari Amman Institute Of technology, Erode,India*

[^] Student, Department of Mechatronics, Bannari Amman Institute Of technology, Erode,India

Abstract—**We demonstrate a potentiostat built with a single commercially available integrated circuit (IC) that does not require any external electronic components to perform electrochemical experiments. This is done using the capabilities of the Programmable System on a Chip (PSoC®) by Cypress Semiconductor, which integrates all of the necessary electrical components. This is in contrast to other recent papers that have developed potentiostats but require technical skills or specialized equipment to produce. This eliminates the process of having to make a printed circuit board and soldering on electronic components. To control the device, a graphical user interface (GUI) was developed in the python programming language. Python is open source, with a style that makes it easy to read and write programs, making it an ideal choice for open source projects. As the developed device is open source and based on a PSoC, modification to implement other electrochemical techniques is straightforward and only requires modest programming skills, but no expensive equipment or difficult techniques. The potentiostat developed here adds to the growing amount of open source laboratory equipment. To demonstrate the PSoC potentiostat in a wide range of applications, we performed cyclic voltammetry (to measure vitamin C concentration in orange juice), amperometry (to measure glucose with a glucose strip), and stripping voltammetry experiments (to measure lead in water). The device was able to perform all experiments and could accurately measure Vitamin C, glucose, and lead.**

Keywords: IR sensor, Opensource, PSoC, Embedded System and MEMS

I. INTRODUCTION

Electrochemistry studies the movement of electrons during chemical reactions and is important for numerous fields including for chemistry (analytical chemistry) [1], biology (neurotransmitter release) [2], material science (electrodeposition, anodization) [3], energy storage (batteries) [4], medicine (glucose sensors) [5], and environmental sensing (heavy metal detection) [6]. A chemical reaction with a transfer of charge between molecules is called an oxidation-reduction reaction. An electrochemical reaction occurs when there is a chemical reaction and a transfer of charge to an external source [7]. By measuring the amount of charge moving through the external source, the chemical reaction rate can be determined. This allows for the monitoring of chemical concentrations and reactions by external electronics [8].

The main type of device used to perform electrochemistry is a potentiostat [14]. The basic requirement of a potentiostat is to control the voltage between two electrodes while measuring the current passing between them, this is a 2-electrode configuration for a potentiostat. To make accurate measurements, the electrodes have to pass a current while maintaining a standard / reference voltage between them. Because a current passing through an electrode causes a voltage change that interferes with keeping the voltage between the electrodes constant, a third electrode is often used for a 3-electrode configuration.

As the three electrodes have different roles, different materials can be used for each electrode in the 3-electrode configuration. The working electrode is selected based on the chemical reaction to be studies . The counter electrode is selected to have a large conductivity to supply current and to be stable and not degrade or oxidize during the experiment, while still passing current . For this reason, noble metals are often used, with platinum being especially prominent. As the reference electrode needs to provide a reference voltage, it needs to have a well-known electrode potential, i.e. a known electrical potential between the electrode material and the electrolytes in solution. Common reference electrodes include the saturated calomel electrode and silver / silver-chloride which are stable and have well characterized electrode potentials.

II. LITERATURE SURVEY

Erickson JS, Shriver-Lake LC, Zabetakis D, Stenger DA, Trammell SA. A Simple and Inexpensive Electrochemical Assay for the Identification of Nitrogen Containing Explosives in the Field. Sensors. 2017;17: 1769. pmid:28767088 concluded that the Opamps used in the DStat were selected for this criterion and have a noise of $6.5\, nV/\sqrt{Hz}$ and an offset of < 0.2 mV, in comparison the Opamps of the PSoC 5LP have a noise of $45\, nV/\sqrt{Hz}$ and an offset of up to 12 mV

Samasilp P, Lopin K, Chan S-A, etal concluded that hydrogen peroxide is no longer the detection molecule, glucose-1-dehydrogenase (GDH) can be used as the glucose oxidizing enzyme. Third generation glucose sensors use direct electron transfer between the oxidizing enzyme, such as GDH-PQQ (pyrrolo quinolone quinone), and the electrode using electron conductive hydrogels

Forsberg G, O'Laughlin JW, Megargle RG, Koirtyihann SR .Determination of arsenic by anodic stripping voltammetry and differential pulse anodic stripping voltammetry. Anal Chem. 1975;47: 1586–1592. Concluded that the concentration of glucose most commercially available devices use amperometry, where the current is measured at the working electrode while the electrode is held at a constant voltage [12]. After an initial period, the current measured is proportional to the rate of glucose oxidation, which is diffusion limited. As Fick's first law states, the diffusion rate is proportional to the concentration of glucose, making the current proportional to the glucose concentration [13].

Yoo E-H, Lee S-Y. Glucose Biosensors: An Overview of Use in Clinical Practice. Sensors. 2010;10: 4558–4576. pmid:22399892 compared the microelectrode fabrication, microfluidics and microelectronic systems have resulted in both challenges: in the design/development of potentiostats and significant advances in the capabilities of the potentiostats to collect data at the transient that take place at different time

Baden T, Chagas AM, Gage GJ, Gage G, Marzullo TC, Marzullo T, et al. Open Labware: 3-D printing your own lab equipment. PLoS Biol. 2015;13: e1002086. pmid:25794301 suggests a new novel way for make possible to obtain sample measurements of patients by using wireless communication and under a large distance between patients and professionals of health by using the internet of things technology. This technology offers features such as shortening the sample analysis periods, reducing the size of the final device reaching portability. Thus, it is possible to implant POCT devices in humans for continuous monitoring purposes [7,8].

III. PRIMARY DESIGN AND WORKING

The potentiostat was designed with PSoC Creator 4.1, Cypress Semiconductor, San Jose, California, a free IDE for programming PSoCs. The device used a PSoC 5LP, which has integrated analog components into a single chip with an ARM Cortex-M3 CPU.

A. Voltage control circuit

To control the voltage between the electrodes we use the circuit shown in Fig 1. The device can use an 8-bit voltage digital to analog converter (VDAC) or a 12-bit Dithering VDAC (DVDAC). The DVDAC is comprised of an 8-bit VDAC where the voltage of the DAC is quickly switched between 2 values. This makes the output the weighted average of the values written, which can be used to increase the resolution of the DAC. This switching causes noise on the output of the DVDAC so that a small capacitor (100 nF) has to be placed on its output to smooth out the voltage. Depending if the user has installed the external capacitor or not, they can choose what DAC to use to drive the common electrode by using an analog multiplexer (AMux) to select the DAC. The user interface asks the user if the DVDAC capacitor was installed and programs the device accordingly. The user's choice is then saved in the electrically erasable programmable read-only memory (EEPROM). An operational amplifier (Opamp) is used to buffer the voltage and to provide feedback from the reference electrode . The build in Opamp has a bandwidth of 3 MHz . The device can be operated in the standard 3 electrode mode or in a 2 electrode mode by setting the appropriate channel on the electrode AMux, which can be done through the user interface. This circuit will pass current through the common electrode pin until the voltage on the reference electrode pin is the same voltage as the DAC. The DAC's voltage is set by the firmware depending on the electrochemical parameters inputted into the device.

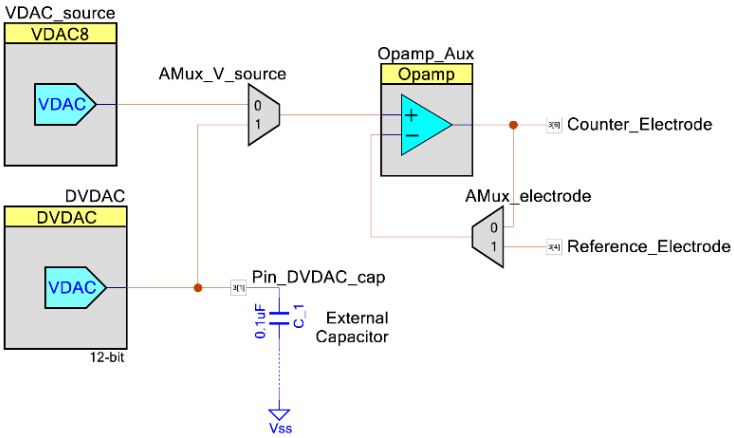

Fig:1 (One of two DACs can be used to control the voltage)

B. Current Measuring circuit

To measure the current, we use a current to voltage converting circuit, a transimpedance amplifier (TIA). The analog voltage from the TIA is then converted to a digital signal using an analog to digital convert (ADC).

Fig.2 shows the circuit used to set the working electrode voltage and to measure the current passing between the common and working electrodes. To allow the device to work from a single power supply while still performing electrochemical experiments at negative potentials, a virtual ground is used. An 8-bit VDAC is used to make a virtual ground at 2.048 V so that the DAC driving the common electrode can make a -2.0 to +2.0 Volts difference between the common and working electrodes, which is a wider range than is needed for most electrochemical experiments.

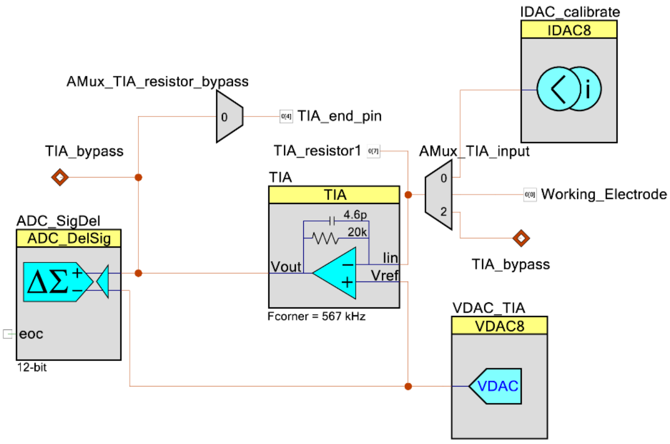

Figure:2 A transimpedance amplifier (TIA) and a DAC are used to set the voltage and measure the current passing through the working electrode

The current that passes through the working electrode is fed into a TIA, with a -3 db cutoff frequency of 567 kHz . As the input impedance of the Opamp is high, the current goes through the resistor of the TIA. This causes a voltage that is the product of the current and the resistance according to Ohm's law (V = I*R). This voltage is then measured by a delta sigma ADC. The ADC is in differential mode, where the voltage is calculated from the difference of the TIA output voltage and the virtual ground voltage. The ADC values are then sent to a computer where they are used to calculate the current that was passed between the counter and working electrodes.

The TIA of the PSoC has a variable impedance that can be controlled by the firmware. The impedance can be one of 8 levels between 20 kilohms and 1 megaohm. To do this the TIA uses switch capacitors and because of how the switch capacitors are manufactured, there can be a large variability in the actual impedance of the TIA (the datasheet says between -25 to +35% of the indicated value). To correct for this the current measuring circuit has a self-calibrating routine. An 8-bit current DAC (IDAC) is used to passed 5 different current levels into the TIA / ADC circuit. The resulting ADC values are then used to calibrate the TIA / ADC signal chain by using a linear interpretation of the calibration data to create the ADC counts to voltage conversion factor and to adjust any voltage offsets. To control when the calibration current or the working electrode current is passed into the TIA component an AMux is used. As the smallest impedance of the TIA is 20 kilohms, the device is limited to 100 µA of current. To give the user the option of increasing the current range, 2 analog pins (P[0][7] and P[0][4]) are made available that the user can place a resistor between with an AMux used to select when the external resistor should be used.

C. Peripherals

Fig:3 shows the other peripherals used by the device. To control the timing of when the DAC voltage should be changed and the ADC values measured, a pulse width modulator (PWM) is used to trigger interrupt service routines (isr). The period and counter values of the PWM are controllable by the user to set different sampling rates. An EEPROM is used to save what DAC the user wants to use. To allow the user to configure the device properly and to export the data from the device to a computer, a Full Speed USB component is used. The USB uses 2 endpoints, an interrupt OUT endpoint that polls the computer ever 10 ms that the user can use to send instructions to the device and a bulk IN that polls the computer every 1 ms that sends the data to the computer to display to the user.

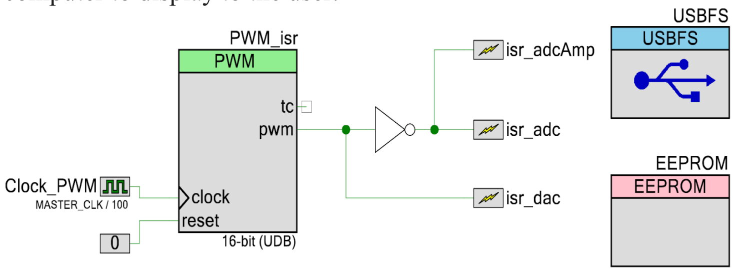

Figure:3 DAC controlling the electrode voltage and when to measure the current, a PWM is used to trigger a set of interrupt service routines (isr).

D. Firmware Development

Application software development is usually done on a cross-development platform such as a Windows PC, Linux box or Mac. The general process is to write the code in an Integrated Development Environment, or IDE, in an embedded language such as C, compile and link the code modules, with libraries if used, and download the binary file to the microcontroller for testing and debugging. This is usually an iterative process. To expand on the process just described, the IDE simply provides a convenient, all-in-one platform where the process of actually entering the source code, compiling, linking and loading can be done in one place. Compiling and linking requires a compiler/linker that can generate binary code suitable to the target microcontroller. Loading can be done in several ways. One, is to have an external device programmer where the target microcontroller is inserted in for loading the compiled binary. The programmed microcontroller is then inserted into its intended HW module for testing. Another way is to build a programming interface in the HW board, and program the microcontroller while it is already attached to its hardware. This method is usually referred to as In-System Programming, or ISP. This is usually referred to as In System Programming. Yet another way, for some microcontrollers, is to download the binary into the microcontroller through one of its peripherals, usually a USART. For that to work, the microcontroller must be running a pre-loaded program called a bootloader that receives the new program, and, in turn, updates itself. Since the bootloader itself is never erased, this means that the microcontroller only has to be externally programmed once with the bootloader code.

E. Gui Development

There are many graphical user interface (GUI) toolkits that you can use with the Python programming language. The big three are Tkinter, wxPython, and PyQt. Each of these toolkits will work with Windows, macOS, and Linux, with PyQt having the additional capability of working on mobile.
A graphical user interface is an application that has buttons, windows, and lots of other widgets that the user can use to interact with your application. The wxPython GUI toolkit is a Python wrapper around a C++ library called wxWidgets. The initial release of wxPython was in 1998, so wxPython has been around quite a long time. wxPython's primary difference from other toolkits, such as **PyQt** or **Tkinter**, is that wxPython uses the actual widgets on the native platform whenever possible. This makes wxPython applications look native to the operating system that it is running on. PyQt and Tkinter both draw their widgets themselves, which is why they don't always match the native widgets, although PyQt is very close.

IV. Methodology Proposed

A. Working

The PSOC acts as the master hub where all the commands are taken as input from the GUI as well as the user and performs the particular selected operation. The major steps involved in the working of the potentiostat are summarized below:

1.Obtain the custom CY8CKIT-059 and plug the USB programmer end (the male end) into a computer. (Win 10 / Linux is preferred over another OS).

2.Download the free program PSoC Programmer from Cypress Semiconductor so that we can map custom hex file into the driver.

3.All the necessary settings, configuration information and other data saved are stored in a binary format which is a HEX file. A HEX file is a hexadecimal source file typically used by programmable logic devices, such as microcontrollers in remote controls, office machines, and automobile engine control systems.

4.Attach wires to pins 0.0 (working electrode), 3.4 (reference electrode), and 3.6 (counter electrode) using either conductive glue or alligator clips.

5.Use a USB cable to connect to the female end of the CY8CKIT-059.

6.A **USB driver** is necessary for the next routine. A driver file is a file that allows a hardware device to communicate with the operating system of a computer.

7.Download the free program Zadig, at http://zadig.akeo.ie/, to install the windows UBS drivers.

8.Select "List all devices" from the options menu in Zadig, select the "Potentiostat" device, select the libusb-win32 driver and click on the Install Driver button.

9. Run the executable file NU.Potentiostat.exe at win terminal or linux.

10.The following are the inputs commands the device will take, all inputs are inputted as ASCII strings.

'I' - Identifies the device, will respond with "USB Test - v04" through the USB

"L|X" - Set electrode configuration to 2 or 3 electrodes. X is the number of electrodes, only 2 or 3 works

"S|XXXX|YYYY|ZZZZZ|AB" - Make a look up table for a cyclic voltammetry experiment. XXXX is the uint16 with the starting number to put in the DAC for the experiment. YYYY is the uint16 with the ending number to put in the dac for the experiment. ZZZZZ is the uint16 to put in the period of the PWM timer to set the sampling rate. A is a char of 'L' or 'C' to make a linear sweep ('L') or a cyclic voltammetry ('C') look up table. B is a char of 'Z' or 'S' to start the waveform at 0 Volts ('Z') or at the value entered in the XXXX field.

'R' - Start a cyclic voltammerty experiment with the last look up table that was inputted. To get the data get the ADC Array 0.

"EX" - Export an ADC array. There are 4 arrays, cyclic voltammetry experiments are stored in the 0 array, the other arrays are used for streaming applications.

"M|XXXX|YYYY" - Run an amperometry experiment. You need to start to read the data the device will start streaming when given this command. XXXX is an uint16 number to set the DAC value to so the electrodes are at the approriate voltage. YYYY is an uint16 of how many data points to collect in each ADC buffer before exporting the data

"FX" - Exprot an ADC array for streamming data where X is the number of the ADC array to get from 0-3.

"A|U|X|Y|Z|W" - Set up the TIA and ADC. U is the ADC configuration to use where config 1 uses a Vref of +-2.048 V and config 2 uses +-1.024 V. X is the TIA resistor value index, a string between 0-7 that sets the TIA resistor value {0-20k, 1-30k, 2-40k, 3-80k, 4-120k, 5-250k, 6-500k, 7-1000k}. Y is the adc buffer gain setting {1, 2, 4, 8}. Z is 'T' or 'F' for if an external resistor is to be used and the AMux_working_electrode should be set according. W is 0 or 1 for which user resistor should be selected by the AMux_working_electrode.

'B' - Calibrate the ADC and TIA signal chain.

"VXY" - Check or set the voltage source. X is 'R' to read the voltage source or 'S' to set the voltage source. When setting the voltage source Y should be '2' for the 12-bit dithering VDAC, all other numbers will default to the 8-bit VDAC.

When reading the voltage source, the device will return the string "VZ" where Z is the voltage source choice selected before.

"S|XXXXX" - set the period value of the PWM used as a timer that starts the isrs to change the DAC and read the ADC. XXXXX is a uint16 that is put into the PWM that set the timing with a sample rate of 240 kHz / XXXXX

"C|XXXXX" - set the compare value of the PWM used as a timer that sets when the DAC changes compared to when the ADC measures.

'X' - Reset the device. Disable all isrs and put the hardware to sleep.

"D|XXXX" - Set the voltage control DAC. XXXX is the value to put in the DAC, which ever one is active.

'H' - Wake up all the hardware.

's' - Short the TIA so the working electrode can sink more current.

'd' - Stop shorting the TIA

B. Methodology

Potentiostat controls the potential of the working electrode and measures the current flowing through it. Why not just two electrodes? One of the reasons is that we cannot measure the potential of the working electrode against a fixed point when we just have two electrodes. Imagine a two electrode system that consists of the already mentioned working electrode and the electrode, which potential should be our fixed reference point, the reference electrode.
We apply a certain potential between these electrodes and an electrochemical reaction happens at the working electrode, but since the circuit needs to be closed and current needs to flow, a reaction that is inverse to the reaction at the working electrode must occur, that is if an oxidation occurs at the working electrode, a reduction must take place at the reference electrode. If a current flows at a constant potential, an electrochemical reaction must happen according to Faraday's law:

$$Q = n \cdot z \cdot F$$

Equation 3.1 | Faraday's Law
This equation says that the charge Q flowing through an electrode is proportional to the amount n of a species that took or gave z electrons at the electrode. F is the Faraday constant and represents the charge of 1 mol electrons. The current I is the charge Q per time t flowing through the electrode:

$$I = Q/t$$

Equation 3.2

The equations' 3.1 and 3.2 combination shows that the current I flowing is connected to the reaction happening at the electrode via the amount n:

$$I = \frac{n \cdot z \cdot F}{t}$$

Equation 3.3
Imagine now that the current is flowing at the reference electrode. At this electrode a species' amount of n is converted. This conversion leads to a change of the surface or the concentration of the solution surrounding the electrode. The Nernst equation shows a clear correlation between the potential E of an electrode and its surrounding:

$$E = E^0 + \frac{RT}{zF} \ln \frac{a_{Ox}}{a_{Red}}$$

Equation 3.4 | Nernst equation
E^0 is the standard potential of the redox couple Red and Ox. R is the gas constant and T the temperature. The activity of the oxidized and reduced form of the species a_{Ox} and a_{Red} in the surrounding solution is not always easy to predict. This often leads to a simplification of the equation:

$$E = E^0 + \frac{RT}{zF} \ln \frac{c_{Ox} f_{Ox}}{c_{Red} f_{Red}} = E^0 + \frac{RT}{zF} \ln \frac{c_{Ox}}{c_{Red}} + \frac{RT}{zF} \ln \frac{f_{Ox}}{f_{Red}} = E^{0\prime} + \frac{RT}{zF} \ln \frac{c_{Ox}}{c_{Red}}$$

Equation 3.5
The two activity coefficients f_{Ox} and f_{Red} are included in the resulting potential $E^{0'}$, which is called the formal potential. Since it contains parameters that depend on the environment, such as temperature and activity coefficients, $E^{0'}$ cannot be listed but needs to be determined for each experiment, if necessary. Most experiments in analytical chemistry are performed at room temperature (295 K). This makes another simplification possible. Out of convenience also the ln will be transferred to the log.

$$E = E^{0\prime} + \frac{RT}{zF} 2.3 \log \frac{c_{Ox}}{c_{Red}} = E^{0\prime} + \frac{0.059\,V}{z} \log \frac{c_{Ox}}{c_{Red}}$$

Equation 3.6
For practical application equation 3.6 is the most used form of the Nernst equation. For many applications one can assume that E^0 is roughly the same as $E^{0'}$, because both of the activity coefficients are close to one.

V. CONCLUSION

In the course of the most recent couple of years there has been a development in making open source research center instruments . The wide spread reception of 3D printers has permitted labs to deliver their own gear, while sharing their plans online for others to utilize and change . This related to the advancement of open-source microcontroller stages (for example Arduino), has made it simpler for analysts to build up their own electronic hardware. The Programmable System on a Chip (PSoC) is another device that can be utilized by the open source local area to create electronic hardware that has numerous advantages contrasted with other microcontrollers. The PSoC 5LP joins a microcontroller with programmable simple parts. This adaptability permits electronic gadgets to be made without making a custom PCB and interfacing various ICs. This significantly lessens the turn of events and creation cost of these gadgets in asset restricted conditions. We exhibited that it is feasible to build up a potentiostat utilizing only a solitary PSoC and showed its capacities by deciding Vitamin C degrees of squeezed orange, showed it tends to be utilized as a solitary chip glucose meter, and that it can decide lead pollution in water. Distinctive electrochemical methods are performed by switching the check out table capacities in lut_function.c and extra strategies, for example, differential heartbeat voltammetry or square wave voltammetry could be modified into the gadget by adding the proper installed capacities. We have made our gadget open source with the goal that it tends to be utilized as a kind of perspective plan.

VI. REFRENCES

[1] B. Bharathi and B. S. Samuel, "Dieter, Fox, Sebastian Thrun and Wolfram Burgard (2013). Probabilistic Robotics. 2005. Using Zigbee," *Int. J. Sci. Eng. Res.*, vol. 1, no. 1–3,

[2] B. P. B. orchate Trupti, "Advances in Robot Kinematics (2020)," *Int. J. Adv. Res. Electr. Electron. Instrum. Eng, Vol. 04, no.05, pp. 3831-3836,*

[3] D. Mândru., et al (AQTR 2010)"Robot cells and production lines. en.ros.org/wiki/SLAM

[4] Lionel M. Ni and Dian Zhang (2011), "RFID-based localization and tracking technologies," IEEE wireless communication, Vol. 18, no. 2, pp. 45–51.

[5] Erickson JS, Shriver-Lake LC, Zabetakis D, Stenger DA, Trammell SA. A Simple and Inexpensive Electrochemical Assay for the Identification of Nitrogen Containing Explosives in the Field. Sensors. 2017;17: 1769. pmid:28767088

[6] Samasilp P, Lopin K, Chan S-A, Ramachandran R, Smith C. Syndapin 3 modulates fusion pore expansion in mouse neuroendocrine chromaffin cells. Am J Physiol—Cell Physiol. 2014;306: C831–C843. pmid:24500282

[7] Dejang N. Fabrication NiAl/Cu Composite Powder for Thermal Spray Coating. Appl Mech Mater. 2017;866: 240–243.

[8] Dobbelaere T, Vereecken PM, Detavernier C. A USB-controlled potentiostat/galvanostat for thin-film battery characterization. HardwareX. 2017;2: 34–49.

[9] Heller A, Feldman B. Electrochemical Glucose Sensors and Their Applications in Diabetes Management. Chem Rev. 2008;108: 2482–2505. pmid:18465900

[10] Forsberg G, O'Laughlin JW, Megargle RG, Koirtyihann SR. Determination of arsenic by anodic stripping voltammetry and differential pulse anodic stripping voltammetry. Anal Chem. 1975;47: 1586–1592.

[11] Wipf DO, Kristensen EW, Deakin MR, Wightman RM. Fast-scan cyclic voltammetry as a method to measure rapid heterogeneous electron-transfer kinetics. Anal Chem. 1988;60: 306–310.

[12] Robinson DL, Venton BJ, Heien MLAV, Wightman RM. Detecting Subsecond Dopamine Release with Fast-Scan Cyclic Voltammetry in Vivo. Clin Chem. 2003;49: 1763–1773. pmid:14500617

[13] Franke W, Deffner M. Zur Kenntnis der sog. Glucose-oxydase. II. Justus Liebigs Ann Chem. 541: 117–150.

[14] Yoo E-H, Lee S-Y. Glucose Biosensors: An Overview of Use in Clinical Practice. Sensors. 2010;10: 4558–4576. pmid:22399892