Supporting Information for

Building a Microcontroller based potentiostat: A Inexpensive and versatile platform for teaching electrochemistry and instrumentation.

Gabriel N. Meloni*

Instituto de Química

Universidade de São Paulo

São Paulo, SP, Brazil

Av. Profesor Lineu Prestes, 748

05508-000

*e-mail: gabriel.meloni@usp.br

*To whom correspondence should be addressed

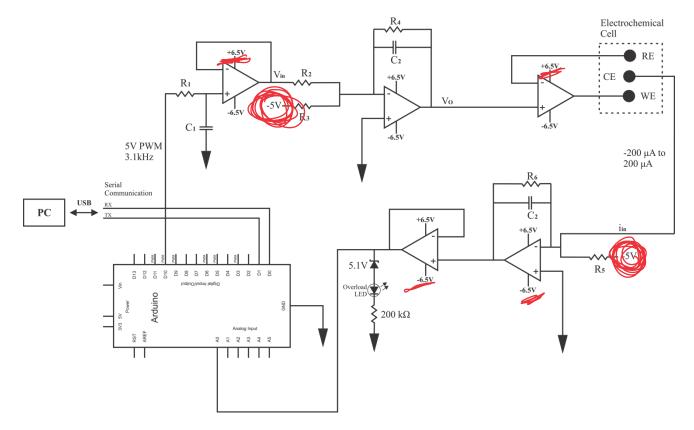


Figure S1. Full schematic design of the potentiostat including the Arduino board pin connections.

Table S1. Component values used during the electrochemical experiments on the main manuscript. Components are labeled as on Figure S1.

Component label on Figure S1	Component Value
R1	$10k\Omega$
R2	510Ω
R3	$lk\Omega$
R4	200Ω
R5	$24k\Omega$
R6	$12k\Omega$
C1	470nF
C2	100nF

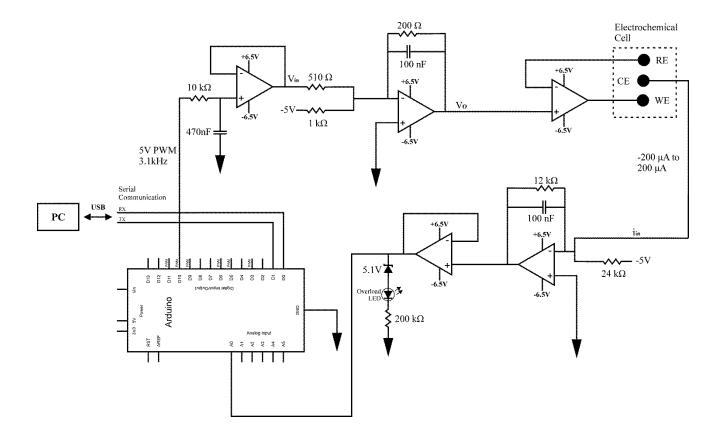


Figure S2. Full schematic design of the potentiostat including the Arduino board pin connections. All the components values are the ones used on the electrochemical experiments.

Power supply

Most operational amplifiers (Op-Amp) such as the LM324 (Texas Instrument) used on this report are usually powered by symmetrical power supplies *i.e.* they need to be powered with both a positive and negative voltage (symmetrically) with respect to ground.

Although this is not true for all Op-Amp applications, it is true for the proposed circuit. The +/- 6.5V supply shown on figure S1are designed to allow for a +/- 5V output on the Op-Amp (after the internal voltage drop, commonly 1.5V) which is within the microcontroller capabilities as described further. This is not necessary and is intended to be a failsafe to avoid damage to the microcontroller, as it is the 5.1V Zener diode connected between the output of the Analog to digital converter (ADC) (Figure S1 and S2) and ground. The LM324 quad Op-Amp can be powered with a dual power supply up to +/- 16V with respect to common ground and thus can be powered by a PC ATX power supply +12V and -12V rails. ATX power supplies are readily available and can be often salvage from old PC without adding any cost to the project.

The -5V supplied to the summing amplifier and current to voltage converter (Figure 1ii (A) and 1ii (C) on the main manuscript) should be stable and precise, as any fluctuation on this voltage will cause an offset on both the applied potential to the electrochemical cell and the current read from it. A voltage regulator such as the LM79L05 can be used to provide a stable -5V from the -12V rail of the ATX power supply.

Digital to analog converter (DAC).

As the Arduino Uno boards do not have a true digital to analog converter (DAC) but only pulse-width modulation (PWM) and for a cyclic voltammetry experiment, a potential ramp should be applied on the potential controller (Figure 1ii (B) of the main manuscript), the square wave generated by the PWM must be converted into a potential ramp. One alternative is to use an RC filter to convert PWM values into true analog values. The drawback of using this approach is that for a Uno board the PWM has an 8-bit resolution,

generating only 256 discreet potential values. This might result in poorly defined voltammograms, especially if performing experiments with less than the maximum and minimum potential limit of the equipment. The summing amplifier as seen in Figure 1ii (A) gives those limits. Besides the resolution problem, most Arduino boards have low frequency PWM signal, ranging from 400 Hz to 960 Hz², resulting in a high time constant for the RC filter. These frequencies are determined by an integer divider on the internal clock of the board, meaning that the frequency can be changed by changing the divider value, resulting in frequencies up to 3.1 kHz, much more suitable for the intended application. Table S2 lists the truth table for the PWM based DAC.

Table S2. Truth table for the summing amplifier, showing its voltage output as a function of the DAC voltage/PWM level.

Input	Output
(V/PWM level)	(V)
0/0	1
2.5/127	0
5/255	-1

The PWM voltage of the Uno board is 5 V and the DAC can only provide voltages from 0 to 5 V. Thus, a summing Op-Amp is needed for cyclic voltammetry experiments as we are interested to vary the potential between negative and positive values. As most of the teaching experiments in electrochemistry are performed in water and the electrochemical window for water is not greater than 1.5 V for most working electrode (WE) materials, there is no point in sweeping the potential up to 5 V. Thus, the summing amplifier can be designed to output voltages in a more usable range. As the 8-bit resolution will be used in

the whole span of the potential window, the design of the summing amplifier is a compromise between the potential resolution and potential window width. The width of the window can be adjusted by changing the values of V_{b1} , R_2 , R_3 , and R_4 (Figure S1). Applying Kirchhoff's law and Ohm's law on the inverting input of the summing amplifier, it can be easily seen that the relation between V_O , V_{in} , V_{b1} , R_2 , R_3 , and R_4 is given by

$$V_0 = -R_4(\frac{V_{in}}{R_3} + \frac{V_{b1}}{R_2}).$$

Figure S3 shows a plot of the output of the DAC and summing amplifier for the setup described in Figure S1.

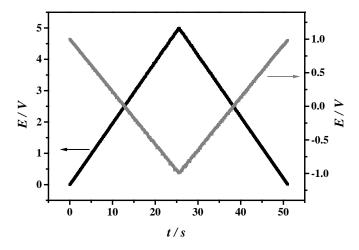


Figure S3. E vs. t plot of the DAC output (black line) and summing amplifier output (grey line).

-Scan rate

The maximum scan rate for the designed device is dependent on the rise time of the RC filter used on the ADC. In addition, the potential window and resolution will affect the maximum scan rate. All those parameters can be changed allowing for some experimental setup flexibility. As the DAC bit resolution is fixed (8-bit) the DAC can generate 256

different levels. With a potential window of 2V (from -1V to 1V) as used for the electrochemical experiments, the DAC resolution is 0.0078V. With a DAC RC filter rise time of 0.01s ($10k\Omega$ resistor and 470nF capacitor and 3.1kHz PWM) the maximum scan rate on the setup used for the electrochemical experiments would be 0.780 Vs⁻¹. The maximum scan rate of the device is defined by:

$$v_{max} = \left(\frac{E_w}{256} / RC_t\right)$$

Where:

v_{max}	Maximum scan rate value (Vs ⁻¹)
E_w	DAC potential window width (V)
RC_t	DAC RC filter rise time (s)

Analog to digital converter (ADC)

The current reading part of the equipment is highlighted in Figure 1ii (C) in the main manuscript and it consists of an Op-Amp in a current to voltage converter setup (transimpedence amplifier) connected to the counter electrode (CE). The current to voltage converter (CVC), as its name suggests, converts the current that flows through the electrochemical cell into a potential that the microcontroller can read. To avoid any damage to the microcontroller the Op-Amps are supplied with +6.5 V, which is within the microcontroller limits. This means that an overload in the current reading will only result in a saturated amplifier and not cause damage to the equipment. The current limit is given by the resistor R_6 (Figure S1) connected to the transimpedence amplifier feedback loop. Using

the property of Op-Amps^{3,4} and Ohm's law, one can easily see that the current limit is given by

$$V_{CVC} = i_{in} \times R_6$$

where V_{CVC} is the output voltage of the converter. The potentiostat was designed to use the maximum dynamic range of potential reading form the microcontroller (0-5 V) and engineered taking into account that the Arduino Uno board does not read negative potentials, meaning that a value of 0 A on the current to voltage converter should result in 2.5 V (Table S3). This was achieved by the addition of a bias potential on the inverting input of the amplifier.

Table S3. Truth table of the current to voltage converter, showing its voltage output and ADC level as a function of the current flowing through the counter electrode.

Input	Output	ADC level
(μΑ)	(V)	
-200	0	0
0	2.5	511
200	5	1023

Table S4. Current and voltage limits for the potentiostat used during the experiments performed in the main manuscript.

	Min.	Max.
Potential (V)	-1	1
Current (µA)	-200	200
Voltage compliance (V)	-5	5

Scan rate (Vs ⁻¹)	0.780

Arduino sketch

Basic Arduino script used to run electrochemical experiments. The latest Arduino IDE can be downloaded from: https://www.arduino.cc/en/Main/Software.

The script presented below was used to automatically perform cyclic voltammetry experiments at different scan rates as seen in the diffusion coefficient determination section of the main manuscript. All the parameters (scan rates and potential window) can be defined in the software. This shows the flexibility and versatility of the design (both hardware and software) in allowing to perform multiple experiments and automating repetitive procedures.

```
//Script starts
include <LiquidCrystal.h>
LiquidCrystal lcd(8, 9, 4, 5, 6, 7);

int a = 10;
int val = 0;
float ct = A0; //ADC
float c = 0;
int n = 0;
float Potstep = 0.0078; // fixed due to the DAC resolution
int vevals[] = {100,20,50,100,200,250,300}; //multiple scan rates values (mV/s)
int const count = 6;
long intervalos[count];
void setup() {

TCCR1B = TCCR1B & B11111000 | B00000001; //Set dividers to change PWM frequency
Serial.begin(9600);
```

```
pinMode(a,OUTPUT);
 pinMode(ct,INPUT);
}
void loop() {
for(int pos = 0; pos < count; pos++){</pre>
 intervalos[pos]=(1000000L/((vevals[pos])*128L));
}
 for(int pos = 0; pos <= count; pos++){</pre>
 n = 0;
  while(n \le 1){
//Start the forward scan
for(val = 0; val <= 255; val++){
  analogWrite(a,val);
  Serial.print(val);
  delay(intervalos[pos]);
  //c = ((0.00195*(analogRead(ct))-1)*1000); // Current reading outputs in uA!!!
  c =analogRead(ct);
  Serial.print(" ");
  Serial.print(c);
  Serial.print(" ");
  Serial.print(n);
  Serial.print(" ");
  Serial.print(vevals[pos]);
  Serial.print(" ");
  Serial.println(intervalos[pos]);
  }
//Start the reverse scan
 for(val = 255; val >= 0; val--){
  analogWrite(a,val);
  Serial.print(val);
  delay(intervalos[pos]);
  //c = ((0.00195*(analogRead(ct))-1)*1000); // Current reading outputs in uA!!!
```

```
c =analogRead(ct);
Serial.print(" ");
Serial.print(c);
Serial.print(" ");
Serial.print(" ");
Serial.print(vevals[pos]);
Serial.print(" ");
Serial.println(intervalos[pos]);
}
n=n+1;
}
//Script ends
```

Data acquisition

Aiming to provide a flexible and free solution that is supported by the open source and DIY community, the proposed device uses the Arduino IDE serial communication capabilities to receive and send data. The data can be sent by the Arduino board as text in a tab separated value (tsv) format that can be further manipulated using any data processing software or as a graph on Arduino IDE 1.6.6 and above. The simple serial communication enables for user with programming skills to make their own communication programs on their preferred programing language.

Diffusion coefficient calculation

$$i_P = 268,600n^{\frac{3}{2}}AD^{\frac{1}{2}}Cv^{\frac{1}{2}}$$

Randles–Sevcik equation at 25°C⁵ where:

i_P	Peak current	Ampere
n	Number of electrons involved on the reaction	
A	Area of the electrode	cm ²
С	Concentration of the electroactive species	mol/cm ³
v	Scan rate	V/s
D	Diffusion coefficient	cm ² /s

Bill of materials.

Table S5. Material list for the fabrication of 1 unit of the proposed potentiostat. Items marked with '*' represent items to be used only if not using an adjustable power supply.

Component	Quantity (Unities)
LM79L05(Voltage regulator)*	1
LM79L08(Voltage regulator)*	1
LM78L08(Voltage regulator)*	1
5V1 Zener diode	1
200Ω resistor	1
510Ω resistor	1
$lk\Omega$ resistor	1
$10k\Omega$ resistor	1
$12k\Omega$ resistor	1
$24k\Omega$ resistor	1
100nF ceramic capacitor	1
470nF ceramic capacitor	1
3 way screw terminal	1

2 way screw terminal	2
LM324 (quad Op-Amp)	2
Arduino Uno board	1

Device construction

Figure S4 show multiple angles of the device used for all the measurements presented so far. The device was fabricated using a breadboard type of construction providing a high degree of customization and flexibility on the potentiostat parameters (potential window, current range, among others).

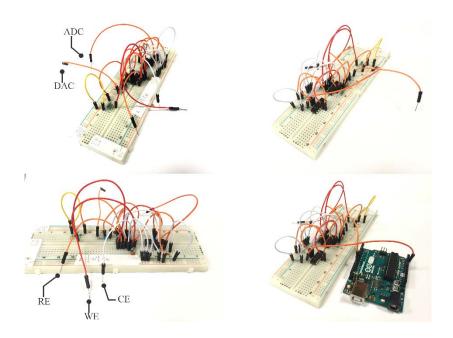


Figure S4. Pictures of the device used on the experiments showing its breadboard construction. Highlighted are the jumper wire connections to the ADC and DAC (top left image) and to the reference, counter and working electrodes (bottom left picture).

Figure S5 shows an alternative construction for the potentiostat using a custom etched printed circuit board (PCB). The PCB design is based on "Arduino shield" design

making it easy to connect to an Arduino Uno board without the concern of mismatching the pins. The use of a secondary shield (small PCBs on the top pictures) containing R_5 and R_6 allow the current range to be changed on a PCB construction witch is intrinsically less flexible than a breadboard.

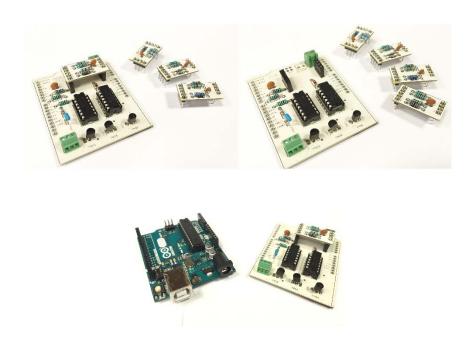


Figure S5. Multiple pictures of the proposed potentiostat design fabricated using a custom etched PCB in an "Arduino shield" configuration. The small PCBs on the top pictures are shield that can be attached to the main PCB to allow for current range changing.

Even though the use of a PCB construction can reduce the electronic noise on the measurements and delivers a more robust device that can still allow for hardware flexibility (using alternatives like the small shields for current range), it is not necessary. A device constructed using a breadboard is still perfect capable of performing precise electrochemical measurement as shown on the results of the main manuscript.

References

- (1) LM324 datasheet http://www.ti.com/lit/ds/symlink/lm324.pdf.
- (2) Arduino Playground PwmFrequency http://playground.arduino.cc/Code/PwmFrequency (accessed Aug 24, 2015).
- (3) Bard, A. J.; Faulkner, L. R. *Electrochemical methods : fundamentals and applications*; 2001.
- (4) Scherz, P. Practical Electronics for Inventors http://www.ee.iitb.ac.in/student/~bhagwan/Basic Electrical Engineering/Practical Electronics for Inventors.pdf.
- (5) Kissinger, P. T.; Heineman, W. R. J. Chem. Educ. 1983, 60 (9), 702.