

EmStat Pico: Embedded Electrochemistry with a Miniaturized, Software-Enabled, Potentiostat System on Module

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Abstract/Introduction

Electrochemistry has miniaturized. Instruments have scaled down from rack mount or desktop machines to handheld devices for point of care or environmental analysis. The next generation of instruments is seeing potentiostats integrated into smaller devices such as wearables, medical devices, or gas monitors. The **EmStat Pico**, a collaboration between Analog Devices and PalmSens BV, is a tiny (30.5 mm × 18 mm × 2.6 mm) system on module (SOM) potentiostat which continues this trend of size reduction. The device is built using Analog Devices technology, including the [ADuCM355](#), [ADP166](#), [ADT7420](#), and [AD8606](#).

Electrochemical sensor system development requires a knowledge of firmware, analog and digital electronics, and a familiarity with electrochemistry. This combination of knowledge is often not present in engineering departments. The EmStat Pico module allows the designer to skip the learning curve and shortcut development time by facilitating the integration of standard electrochemical measurements such as linear sweep voltammetry (LSV),

squarewave voltammetry (SWV), or electrical impedance spectroscopy (EIS) into a product with minimal development time and effort. Given the increasing competition in the electrochemical sensors market, the module gives the developer a strong time to revenue advantage.

This article shows the ease of integration of the device into a system and demonstrates the range of applications of the potentiostat module by detailing three different electrochemical measurements: OCP (pH), cyclic voltammetry, and EIS.

System Integration

The EmStat Pico is designed to be integrated into any microcontroller-based system using just four wires (5 V, ground, transmit, receive). Figure 1 shows example setups, firstly using an Arduino MKR as a master controller, and secondly using a USB to UART converter to interface to a PC. In both setups, the EmStat Pico is connected with a screen printed electrode (SPE) for common electrochemical measurements such as cyclic voltammetry (CV).

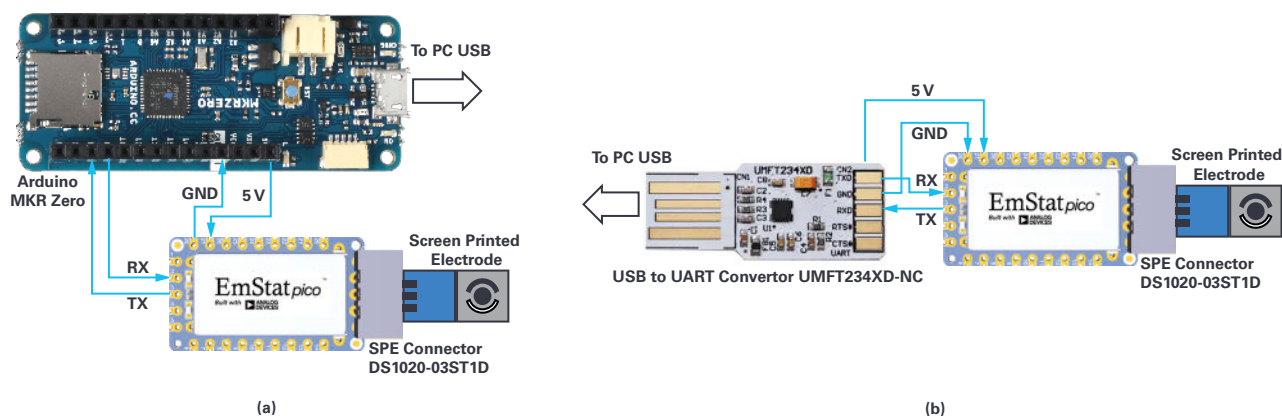


Figure 1. EmStat Pico system integration (a) controlled via an Arduino MKR and (b) controlled directly from a PC via a USB to UART converter.

Development Board

The [EmStat Pico development board](#) shown in Figure 2 breaks out the SOM connections and adds a range of functionality including: battery power and SD card for standalone operation, USB and Bluetooth® communication options, real-time clock (RTC) for time-stamping, EEPROM for calibration data storage, and a header for direct insertion of an Arduino MKR.

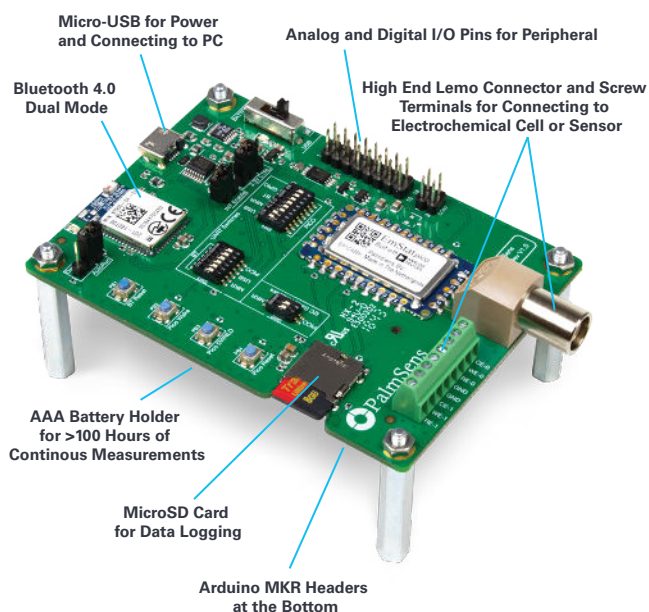


Figure 2. EmStat Pico development board.

Software Interface

For laboratory and test bench applications, the EmStat Pico can be operated by [PSTrace](#) PC software via a USB connection.

For OEM applications, communication is via the UART and the master can use the [MethodSCRIPT™](#) EmStat Pico scripting language to control the EmStat Pico. This is a human-readable script for programming the EmStat Pico to run electrochemical techniques and perform other functions such as loops, data logging to SD, digital I/O, reading auxiliary values (for example, temperature), and sleep or hibernate. Method script code can be generated in PSTrace or written manually.

pH Measurement

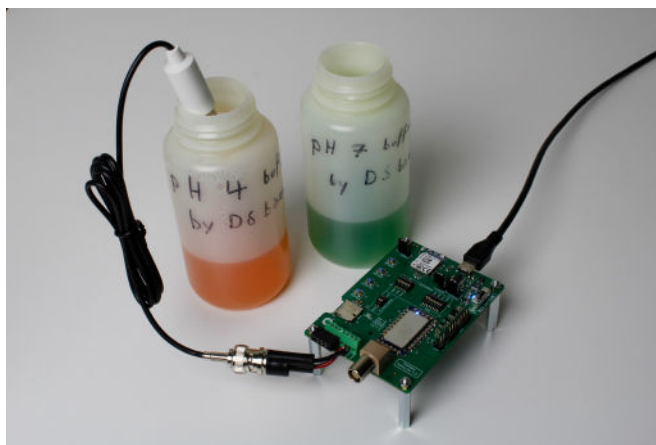
pH with a scale of 0 to 14, (acidic: 0, neutral: 7, basic: 14) is one of the most common electrochemical measurements and is used in many fields from environmental chemistry to medical sensors. The measurement is typically conducted using a glass ion selective electrode (ISE) specific to hydrogen ions, which produces a voltage response, or open circuit potential (OCP). As OCP implies, no current or minimal current should flow in the electrode. Thus, a high impedance input is required for error free measurement. pH electrodes can have settling times up to 30 seconds and measurements are strongly temperature dependent.¹

Typical Measurement Parameters:

- ▶ Voltage response: -59.16 mV/pH unit at 25°C
- ▶ Resolution: ± 0.02 pH units, thus voltage resolution < 1.18 mV
- ▶ Temperature dependency: 0.2 mV/pH unit/ $^{\circ}\text{C}$
- ▶ Required input impedance: > 100 G Ω

Setup Equipment:

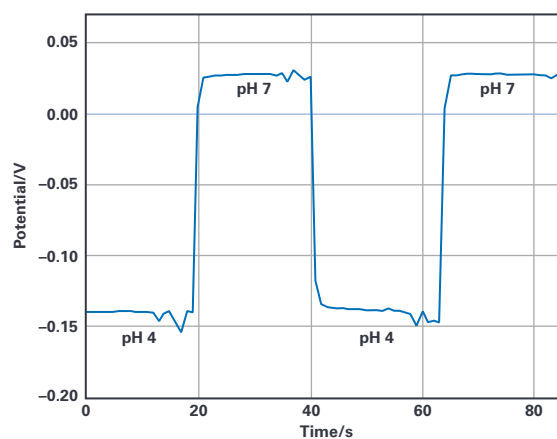
- ▶ EmStat Pico on development board
- ▶ pH electrode: [Votcraft PE-03](#)
- ▶ Buffer solution: [pH 7](#)
- ▶ Buffer solution: [pH 4](#)



Signal	Dev Board Pin	pH Electrode
RE_0	Con 4 pin 6	Inner core
WE_0	Con 4 pin 7	Outer shield

Figure 3. pH measurement setup of EmStat Pico dev board.

The pH electrode was connected to the RE_0 input of the EmStat Pico dev board and referenced to WE_0. Note: this orientation produces an inverted voltage response. The RE_0 input is buffered with an AD8606 op amp on the EmStat Pico to achieve an input impedance > 1 T Ω . The potential on RE_0 Vs WE_0 was recorded for a period of 2 minutes while the electrode was transferred between pH 4 and pH 7 buffers every 20 seconds. After removing the ISE from one buffer, it was rinsed with demineralized water before immersing it into the other buffer.



pH Standard	Potential
4	-0.14 V
7	$+0.03$ V

Figure 4. pH measurement on EmStat Pico dev board.

The difference between the potential at pH 4 and pH 7 was 0.17 V, this means the slope of the linear relationship between potential and pH is 56.7 mV/pH. This demonstrates a sufficient sensitivity considering the theoretically ideal value of 59.16 mV/pH unit at 25°C .

Cyclic Voltammetry

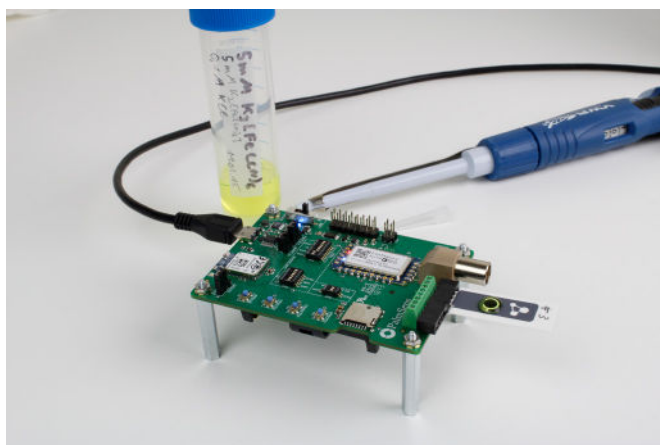
Cyclic voltammetry is a technique where a voltage ramp—for example, -1 V to $+1\text{ V}$ —is applied to an electrode in a solution and then reversed to $+1\text{ V}$ to -1 V , while measuring the current through the electrode. This cycle allows the measurement of anodic and cathodic currents due to oxidation and reduction of chemical species at the electrode solution interface.² The technique is routinely used for detection and quantification of electroactive species—for example, metal complexes such as Prussian blue (a common dye).

Typical Measurement Parameters:

- ▶ Applied voltage: -1 V to $+1\text{ V}$
- ▶ Step size: 10 mV
- ▶ Current response: $\pm 10\text{ nA}$ to $\pm 1\text{ mA}$
- ▶ Ramp rate: 100 mV/s

Setup Equipment:

- ▶ EmStat Pico on a development board
- ▶ Screen printed electrodes (SPEs): [LP-3.13.WP.350](#) by LanPrinTech
- ▶ SPE connector: [DS1020-03ST1D](#)
- ▶ Potassium ferricyanide $\text{K}_3[\text{Fe}(\text{III})(\text{CN})_6]$
- ▶ Potassium ferrocyanide $\text{K}_4[\text{Fe}(\text{II})(\text{CN})_6]$
- ▶ Potassium chloride ClK



Signal	Dev Board Pin	SPE Electrode
RE_0	Con 4 pin 6	RE
WE_0	Con 4 pin 7	WE
CE_0	Con 4 pin 8	CE

Figure 5. Cyclic voltammetry setup of EmStat Pico development board.

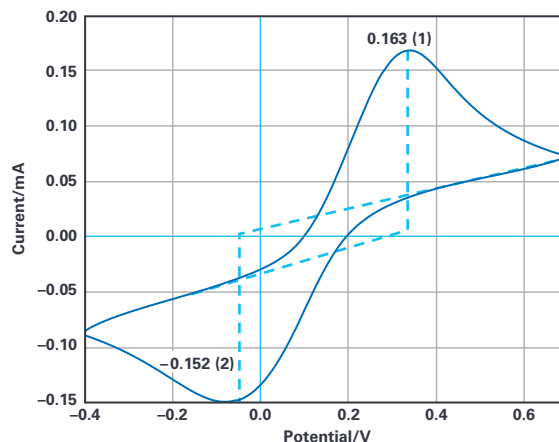
A solution of potassium ferricyanide $\text{K}_3[\text{Fe}(\text{III})(\text{CN})_6]$ and potassium ferrocyanide $\text{K}_4[\text{Fe}(\text{II})(\text{CN})_6]$ (both 5 mmol/L) at a 1:1 molar ratio with 0.1 mol/L potassium chloride as a supporting electrolyte was prepared in distilled water.

The ion $[\text{Fe}(\text{II})(\text{CN})_6]^{4-}$ can be oxidized to $[\text{Fe}(\text{III})(\text{CN})_6]^{3-}$ by a positive electrical potential and then $[\text{Fe}(\text{III})(\text{CN})_6]^{3-}$ can be reduced to $[\text{Fe}(\text{II})(\text{CN})_6]^{4-}$ by a negative electrical potential. This reversible redox reaction makes this solution suitable for demonstration of a CV measurement.

An SPE connector was placed in the PSTAT_0 channel using the screw terminals (CON4) of the EmStat Pico development board. A $200\text{ }\mu\text{L}$ drop of the ferricyanide: ferrocyanide solution was placed on the active surface of the SPE.

The EmStat Pico was setup to run a CV on PSTAT_0 with the following measurement parameters—applied voltage: -0.4 V to $+0.7\text{ V}$; step size: 10 mV ; ramp rate: 100 mV/s . Data was recorded using PSTrace.

Results



	Potential	Current
Oxidation	+340 mV	+0.163 mA
Reduction	-80 mV	-0.15 mA

Figure 6. Cyclic voltammetry of 5 mM ferricyanide: ferrocyanide on an SPE using PSTAT_0 of the EmStat Pico.

The cyclic voltammogram in Figure 6 shows a current peak of $+0.163\text{ mA}$ at an applied potential of $+340\text{ mV}$ due to the oxidation of $[\text{Fe}(\text{II})(\text{CN})_6]^{4-}$ to $[\text{Fe}(\text{III})(\text{CN})_6]^{3-}$. The negative current peak of -0.15 mA , which occurs at -80 mV , is due to a reduction where the process is reversed. The magnitude of the current is proportional to the concentration of the electroactive species that makes this technique suitable for sensing applications. The average of the peak potentials (180 mV) is the formal potential; that is, the potential where the dominance of reduction or oxidation reaction changes.

EIS

Electrical impedance spectroscopy (EIS) is commonly used to examine interfacial chemistry at surfaces such as corrosion interfaces or battery electrodes. This is typically performed by applying a small sinusoidal potential and measuring the current response at frequencies ranging from below 1 Hz to MHz .³

An electrochemical interface can be modeled with a combination of electrical circuit elements. The simplest model is a Randles circuit that contains two resistors and a capacitor. The Warburg element, which represents diffusion, is omitted as it has no equivalent electrical circuit element. The PalmSens dummy cell has three test circuits, including a Randles cell with the nominal values shown in Figure 8c. Here, R_s represents the solution (electrolyte) resistance, C_{dl} represents the double layer (interface) capacitance, and R_{ct} represents the charge transfer (interface) resistance.

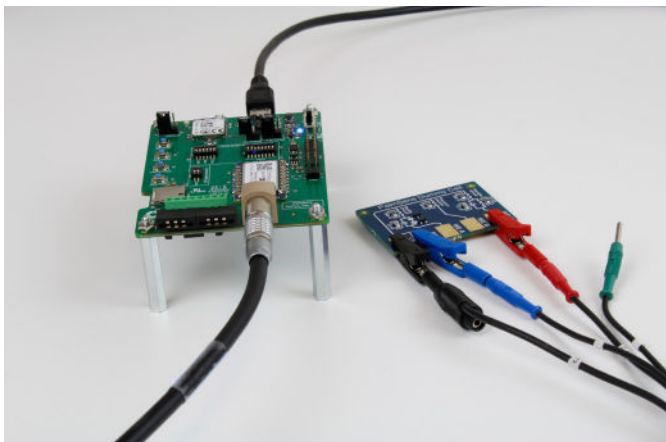
EIS data is typically presented as a Nyquist or a Bode plot and then mathematical circuit fitting is used to identify the values of the elements of the equivalent circuit.

Typical measurement parameters:

- ▶ Excitation voltage: 10 mV p-p sine
- ▶ DC offset voltage: 100 mV
- ▶ Frequency range: 0.1 Hz to 100 kHz
- ▶ Current response: $\pm 100\text{ nA}$ to $\pm 1\text{ mA}$

Setup Equipment:

- ▶ EmStat Pico on development board
- ▶ Sensor cable: [PalmSens sensor cable](#)
- ▶ Randles equivalent circuit: [PalmSens dummy cell](#)

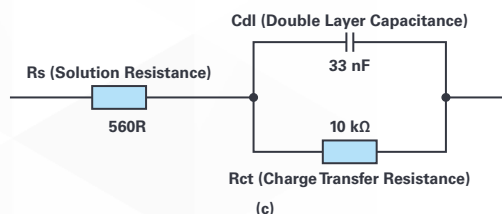
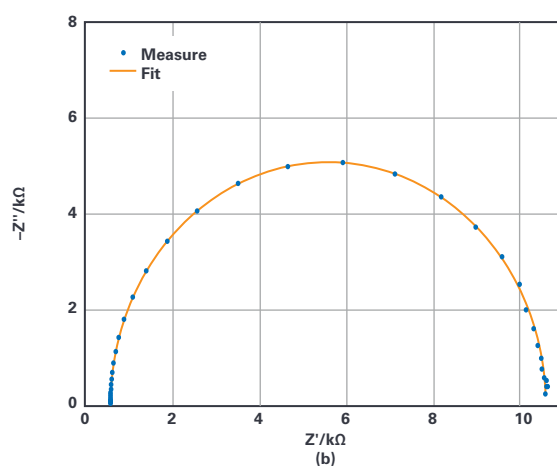
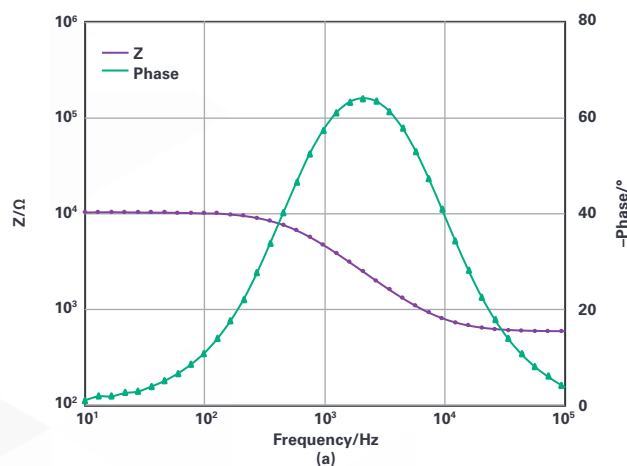


Signal	Dev Board Pin	Cable Color	SPE Electrode
RE_0	Con 8 pin 1	Blue	RE
WE_0	Con 8 pin 5	Red	WE_C
CE_0	Con 8 pin 3	Black	CE

Figure 7. Electrical impedance spectroscopy (EIS) setup of EmStat Pico development board.

The sensor cable was inserted into CON8 of the EmStat Pico development board and the crocodile clip connections were attached to the Randles dummy cell, as shown in Figure 7.

The EmStat Pico was setup to perform an EIS measurement on PSTAT_0 with the following parameters: dc voltage: +1 V; sine: 10 mV p-p; frequency range: 10 Hz to 200 kHz.



A PStace [equivalent circuit fitting](#), which used the Levenberg-Marquardt algorithm, was used to calculate the values of the electrical elements in the circuit.

Results

Figure 8a shows the Bode plot of the Randles circuit in Figure 8c. At low frequency, the 10 kΩ resistance is dominant as the capacitor effect is small. At higher frequencies, the impedance drops to match the solution resistance as the capacitor becomes almost a perfect short.

Figure 8b shows the Nyquist plot of the data in blue and the theoretical model fitted to the data in orange. The values of the equivalent circuit elements calculated from the model are presented in Figure 8d. These match closely with the nominal values of the dummy cell. Note: resistor tolerance is 0.1%, capacitor tolerance is 5%.

Conclusion

The EmStat Pico is a versatile, user-configurable potentiostat capable of performing most common electrochemical measurements. It is presented in a small form-factor system on module package suitable for integration into miniaturized sensing systems. The device is built on Analog Devices technology, including the ADuCM355, AD8606, ADT7420, and ADP166.

References

- ¹ Tim Meirose. *Essentials of pH Measurement*. Thermo Fischer Scientific, 2019.
- ² Allen J. Bard and Larry R. Faulkner. *Electrochemical Methods: Fundamentals and Applications, Vol. 2*. New York: John Wiley & Sons, Inc., December 2000.
- ³ Evgenij Barsoukov and J. Ross Macdonald. *Impedance Spectroscopy: Theory, Experiment, and Applications*. John Wiley & Sons, Inc., March 2005.

Circuit Parameter	Nominal	Calculated
Rs	560 Ω	560.5 Ω
Rp	10 kΩ	10.01 kΩ
Cdl	33 nF	33 nF

(d)

Figure 8. EIS results of EmStat Pico measuring the PalmSens dummy Randles circuit are shown by (a) a Bode plot, (b) a Nyquist plot with a fitted model, (c) a Randles circuit model, and (d) circuit parameters calculated from the fitted model.

About the Authors

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Brian Coffey graduated from the University of Limerick in 1999 with a Bachelor of Engineering in computer engineering, and he has over 20 years experience in the semiconductor industry. He has held several engineering, engineering management, and marketing management roles, and is currently a product marketing manager in the Molecular Sensors Group at Analog Devices in Limerick, Ireland. Brian received his M.B.A. from the University of Limerick in 2011. In addition to his role at Analog Devices, he is deputy general manager of MIDAS, the Irish Microelectronics Association. Brian enjoys coaching the Irish sports of hurling and Gaelic football in his spare time. He can be reached at brian.coffey@analog.com.

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