I. Supplementary material

I.I. Embedded Potentiostat System (EPS)

The EPS prototype includes some modifications to incorporate additional electrochemical techniques. The main aspects are the description of the embedded systems and design patterns for programming. An embedded mixed-signal architecture deals with applications where the acquisition, processing, and manipulation of the variables are necessary [1]. In a potentiostat system, the redox current is the variable to sense, the voltage at the electrodes is the variable to control, and the microcontroller algorithm generates the appropriate waveforms for an electrochemical trial. Thus, a potentiostat application matches with an architecture like this. The main functions to perform by this kind of embedded system are [2]:

- Sensing the analog signals.
- Transmission and reception of data inside and outside of the embedded system.
- Firmware execution.
- Actuation signals generation.

The PSoC from Cypress Semiconductor is one of the icon devices in an embedded mixed-signal architecture [3]. The selection of this device relies on the incorporation of several features in a single chip. Hence, analog, digital, and processing systems are inside of a PSoC with the capacity to address several applications. The main feature of the PSoC is its configurability. That allows to an experimentalist to have new solutions to the most challenging problems [4 -7].

A Full potentiostat system, requires the management of analog and digital signals. A PSoC provides an architecture for the treatment of mixed-signals in one chip [6]. These features bring advantages as fast development times, space reduction, and simplification of the application.

I.II. Prototype Implementation and Architecture

The potentiostat instrument prototype has two main systems: the embedded and the interface system as shown in figure 1. The EPS is responsible for the manipulation of the electrochemical cell sending and receiving data wirelessly. The Potentiostat User Interface System (PUIS) deals with the user and controls the EPS behavior. Both systems constitute a Master/Slave design where the EPS is the slave, and the PUIS is the master.

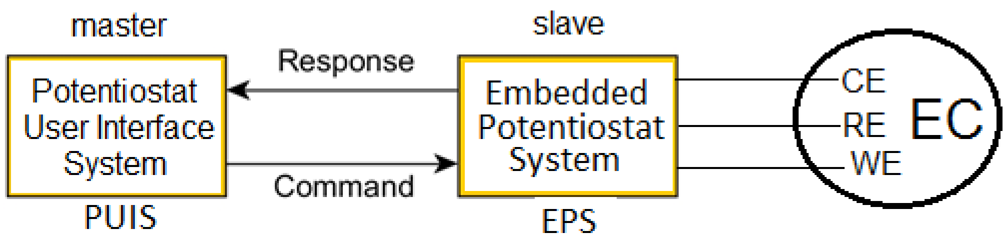


Figure 1. Slave-master scheme: Embedded and User Interface systems (EPS and PUIS) driving the electrochemical cell.

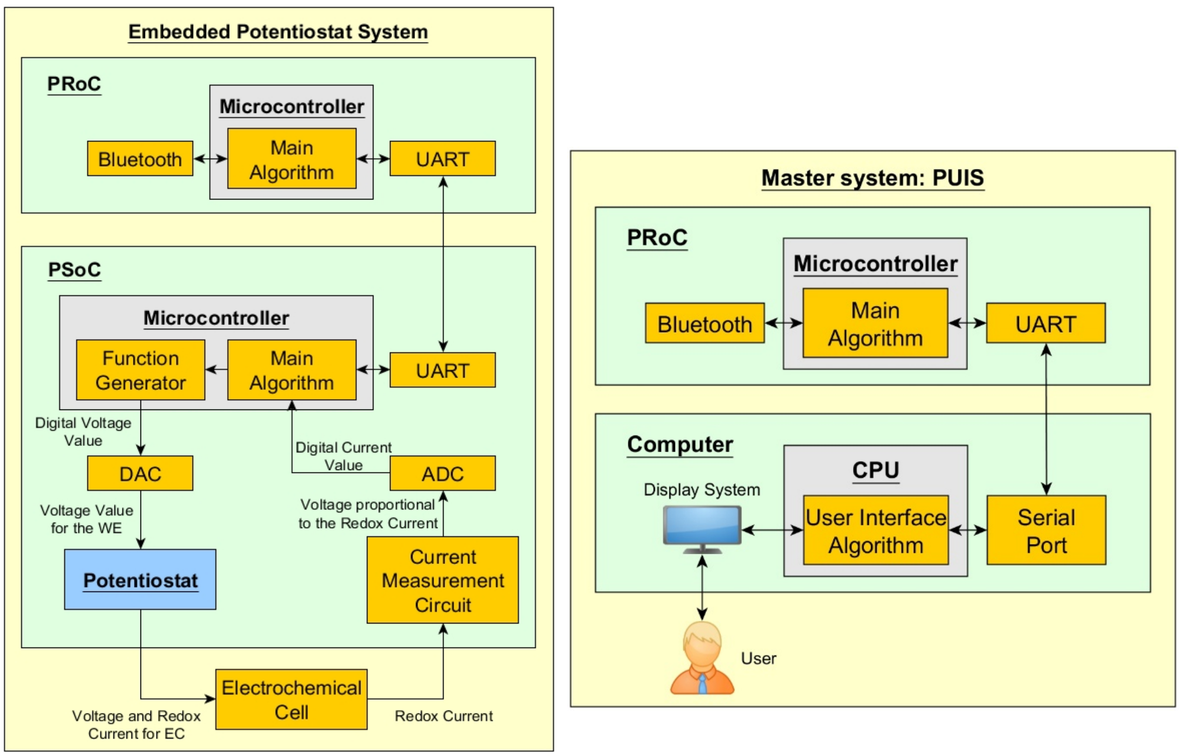
The modular design allows the completion of the research objectives by using a small embedded system as a slave [3]. Also, the modular design is an excellent feature to customize the system. To implement the potentiostat instrument prototype, the master sends commands to the slave, and the slave returns the task response. In this prototype, there is a command for each electrochemical method, and the response is a lot of digital values from the trial. The PUIS focuses on managing the recording and display system, on generating the appropriate waveforms and on sending Redox current/voltage values (according to the test) to the PUIS. This multiprocessing capability allows achieving a full potentiostat system.

The EPS is a set of electronic components small enough to be embedded in a potentiostat system application. This system has three main aspects: Bluetooth, PSoC, and the electrochemical cell as shown in Figure 2(a). The PSoC has analog and digital modules to implement as a potentiostat, a microcontroller, and it executes the firmware. The PSoC analog hardware allows to the designer the development of a basic potentiostat system with all the electronic components needed by the typical potentiostat system. Moreover, the microcontroller has the code for the generation of the waveforms according to the electrochemical technique selected and the parameters to stop a running experiment. The main algorithm of the PSoC has a State Machine design pattern programmed in C language. This design pattern is highly acceptable by programmers because its implementation is very flexible and easy to follow [8]. Also, the modularity of the pattern makes feasible the additions of states to implement more electrochemical methods in the same PSoC. Thus, the state machine is an excellent choice to have a friendly firmware because it is very explicit.

Besides the PSoC, Figure 2(a) shows another chip named PRoC that focuses on Bluetooth communication instead of hardware modules. The addition of this device increases the prototype size. However, this element is extremely important for a successful EPS functionality. Also, the PRoC is one of the best options considering that it comes from the same manufacturer of the PSoC.

The PUIS schematic of Figure 2 (b) uses Bluetooth communication to send commands to the slave. The commands come from a computer with a program and the PUIS is always waiting for any events at the interface to start the electrochemical experiment. Also, it has a recording system to save the data to a computer. Figure 2 (b) shows that the Bluetooth device is out of the computer, and it controls all the communication of the master. Moreover, the Bluetooth version is the BLE 4.2 with a data rate up to 25 Mbps for this prototype [9]. The Bluetooth communication works basically as a bridge allowing the design of a simple communication protocol for sending commands. Thus, it is easy the manipulation of bytes to send tasks to the slave and receive the voltage and the current values.

Recording on a display system is a challenge for any designer. However, the use of advanced design patterns is very helpful. Thus, LabVIEW allows the creation of user interface systems with advanced programming techniques. The algorithm performed by the computer uses a Producer/Consumer and a State Machine design pattern. A later subsection provides more information about these techniques.



(a) Slave system: EPS (b) Master system: PUIS

Figure 2. Modular Potentiostat with slave (EPS)-master structure (PUIS).

I.II.I. Analog and Digital Circuits in the PSoC

The Figure 3 shows the digital schematic circuit of the PSoC which provides a firmware execution in real-time and the communication to the PRoC. The advanced potentiostat circuit with a Trans-Impedance Amplifier (TIA) from Figure 3 has features used to make the electrochemical prototype tests [10, 11]. Moreover, the design of the analog circuitry is very important to provide a good performance in the prototype system. The analog hardware from

Figure 4 relies on the advanced potentiostat circuit with the TIA, and it has some extra features. The Operational Amplifiers marked as Opamp_0 and Opamp_2 control the potential at the WE through the RE, Opamp_1 supplies the energy for the waveform while the DAC throws the waveform values at the proper rate. The Universal Asynchronous Receiver-Transmitter (UART) module communicates with the Bluetooth module to send data and receive commands wirelessly. The Programable Gate Array (PGA) provides a reference voltage of 2.048 V because the RE can be just manipulated in a range of 0 to 4.08 V. Hence, this floating potential gives a chance to work with ±2 V approximately in the electrochemical cell. The TIA and the ADC transform the current into digital values. The DAC brings some restriction to the embedded application. The maximum quantization error is 0.5 mV because every step is of 1 mV. The minimum time for the DAC to change a value at its output is of 4 µs. Hence, the maximum scan rate for the prototype is 250 V/s in a range of 0 to 4.08 V. The DAC needs the digital waveform value in 12 bits to make the conversion. Also, the DAC requires a buffer at the output to keep the right potential and supply the energy to the potentiostat control signal.

The TIA module and the Delta-Sigma Analog to Digital Converter (Δ∑ ADC) define the sensitivity of the current measurement. The TIA has eight resistors to have eight different quantization levels. The maximum current value is obtained by using the values for the operation come from the minimum resistor of the TIA module (20 kΩ) and the ADC voltage range at its input (±1.024 V). However, the missing data needs to be calculated through a characterization.

$$\frac{\pm 1.024\ \mathrm{V}}{20000\ \Omega} = \pm 51.2\ \mu\mathrm{A} \tag{1}$$

The Δ∑ ADC has several features that define the behavior of this module in the prototype. The conversion mode is a single sample. The ADC has 18 bits, and it takes 414 µS approximately to perform one conversion. The clock frequency is around 3071 kHz, but the output rate is slower because it uses oversampling to get a better signal quality. The input range is ±1.024 V, and the ADC has a buffer to avoid any measurement error by impedance mismatching.

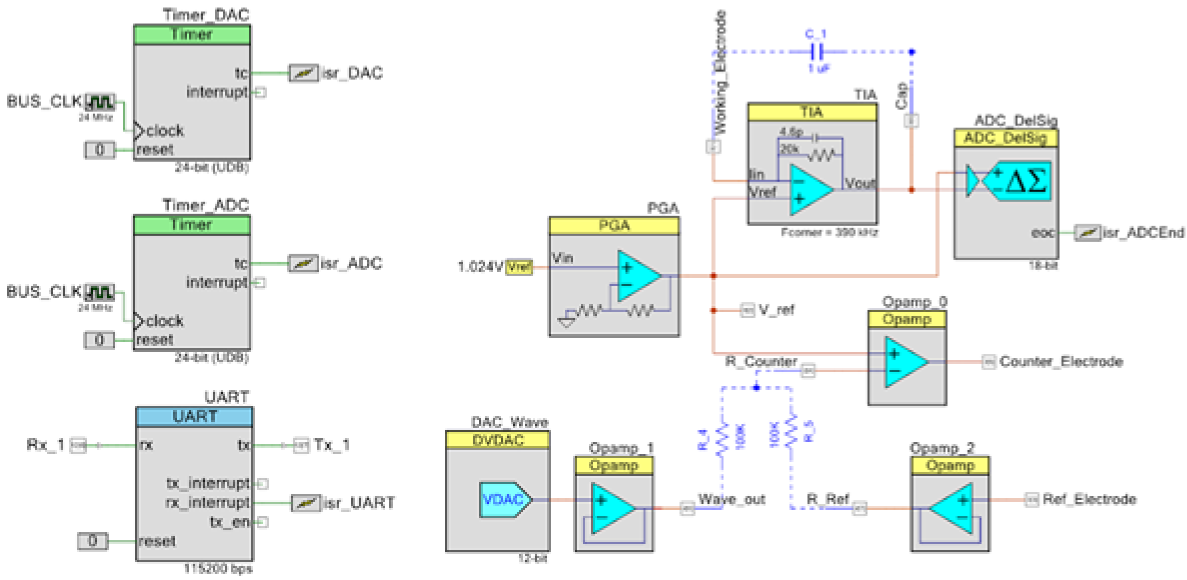


Figure 3. Digital peripherals and analog circuitry of the PSoC

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