Building a Low-cost Standalone Electrochemical Instrument Based on a Credit Card-sized Computer

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A low-cost, standalone electrochemical instrument was built from a credit card-sized computer and inexpensive A/D and D/A converter chips. The instrument is capable of cyclic voltammetry and constant potential electrolysis, with the potential range of −4 to +4 V and the current range of 1 μA to 20 mA.

Keywords Standalone potentiostat, credit card-sized computer

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Introduction

Electrochemistry is becoming an important tool in research and development in the area of materials engineering. Consequently, there is a growing need for education about electrochemistry in laboratories in all areas of chemistry. For this purpose, it is effective for a chemistry laboratory to employ electrochemical equipment that students can handle whenever necessary. Some electrochemical instruments like potentiostats are simple enough to be built in-house from inexpensive electronic parts. Katano reported practical guides for building potentiostats that are suitable for electrochemical education.1–4 More recently, Meloni reported a microcontroller based potentiostat as a low-cost platform for teaching electrochemistry and instrumentation.5 While these reports provide cost-effective solutions for electrochemistry, we still need additional instruments, such as a function generator and an X-Y recorder or a personal computer, to perform electrochemical experiments.

In this article, we wish to report a standalone electrochemical instrument based on a credit card-sized computer. Recent advances in embedded microcontroller electronics led to the development of such card-sized computers. These computers have comparable capabilities with desktop PCs and can be offered at an affordable price. We chose the Raspberry Pi Model A+,6 which is one of the most widely used card-sized computers. The concept of the instrument is shown in Fig. 1. Circuit design, software, and evaluation as electrochemical equipment are described in the following sections.

Circuit Design

The Raspberry Pi does not have a built-in A/D (analog-to-digital) or D/A (digital-to-analog) converter. Therefore, we need to use external devices to interface between the Raspberry Pi and the potentiostat circuit. We used the MCP3204 A/D converter and the MCP4922 D/A converter, both from Microchip Technology Inc. These converters have a 12-bit resolution, which is sufficiently high for basic electrochemical experiments. The converters can communicate with the Raspberry Pi via the SPI interface.

Figure 2 shows the schematic of the digital interface circuit between the Raspberry Pi and the MCP3204 and MCP4922 converters. The converters are powered at 3.3 V. Therefore, the SPI signals match the 3.3 V GPIO (general-purpose I/O) signals of the Raspberry Pi. We did not take the 3.3 V power from the GPIO port of the Raspberry Pi. Instead, we used a dedicated three-terminal regulator (TA48M033F, Toshiba). Use of this regulator was helpful to avoid possible voltage fluctuations caused by the Raspberry Pi.

Figure 3 shows the power supply circuit for the analog part. The circuit is powered by a 5-V line from a switching regulator. Because this 5-V line had a large rippling noise, we treated the 5-V line with a low-dropout voltage regulator NJM2397 (New Japan Radio). After this treatment, the voltage was still sufficiently high (4.6 V), and the ripple noise was effectively

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Fig. 1 The concept of a standalone electrochemical instrument described in this article.
removed. This 4.6-V source is used for generating the ±12 V power supplies for the operational amplifiers (see below). In addition, the same 4.6-V source is also used for generating the reference voltage for the analog-digital conversion (2.495 V). The reference voltage is given by the shunt regulator NJM431L (New Japan Radio). The analog and digital circuits are separated by an EMI filter BNX016-01 (Murata Manufacturing).

The schematic of the potentiostat circuit is shown in Fig. 4. This is essentially the same as in Katano’s report. The modifications are described below. First, the ±12 V power for the operational amplifiers is given by a low-noise DC/DC transformer LT3439 (Linear Technology). This transformer has a very low output noise (typically ±30 μV). Second, the two operational amplifiers (op1 and op5) have the non-inverting input of $V_{\text{ofs}} = 1.13$ V instead of GND. The op1 provides the current of the counter electrode, and the op5 provides the output voltage connected to the A/D converter. The purpose of this modification is that the potentiostat must be able to handle both positive and negative voltages and currents, but the A/D and D/A converters can handle only voltages between 0 to +2.495 V. By using $V_{\text{ofs}}$ as the offset, the voltage of the reference electrode can be controlled in the range from +5.54 to –4.21 V (marked $V_r$ in Fig. 4). The current passing the working electrode is converted to a voltage ($V_{\text{iv}}$) by op3. $V_{\text{iv}}$ can be in the range from +12 to –12 V and is converted to 0 to +2.5 V by op5. The $V_{\text{ofs}}$ value of 1.13 V was chosen so that the same $V_{\text{ofs}}$ can be used by both op1 and op5. The resistors in the inverting inputs of these amplifiers have parallel-connected capacitors (1 nF and 33 nF, respectively). These capacitors work as low-pass filters to remove the oscillation in the output voltage.

As described above, this potentiostat circuit has the potential limit of –5.54 to +4.21 V. This potential range is sufficient for basic electrochemical measurements even when non-aqueous solvents are used. The current limit is determined by the capability of the operational amplifier. We used the NJMOP-07 (New Japan Radio), which has the current limit of 30 mA at 100 ohm load. This limit is also sufficient for small-scale electrochemistry.

Computer Setup and Software

The Raspberry Pi is usually used with a USB keyboard, a mouse, and an HDMI display. However, such a setup will add a substantial cost and occupy too much space on the laboratory bench. Fortunately, some third-party vendors provide a compact liquid-crystal display (LCD) with a touch panel that can be used with the Raspberry Pi. We used a Waveshare 3.2 RPi LCD, but any similar product will do if suitable drivers for the display and the touchpanel are provided for the Raspbian OS (which is the standard OS for the Raspberry Pi).

Instead of using the default graphical user interface (GUI) based on the X Window System, we developed a simple graphic system that draws directly onto the LCD screen. Such a software design requires much less computing power for graphical interface than the X, and spares more processor time for handling electrochemical measurements.

The software was written in LuaJIT, a “just-in-time compiler” variant of the Lua programming language. The LuaJIT
The C language supports "foreign function interface" (FFI), which provides direct binding to the system calls of the underlying operating system. It also allows linking a small helper code written in the C language. Such a helper code was necessary in the present project, because we need to keep the timings of data acquisition as precise as possible (see below).

The flowchart of the data processing is shown in Fig. S1 (Supporting Information). The data acquisition is done in a separate thread. The thread receives the current from the A/D converter, and sends the potential to the D/A converter at the scheduled time. The input/output data are transferred between the main thread and the data-processing thread via a ring buffer.

The data acquisition thread is written in C, and set to run with a higher priority than the main thread (the code snippet is shown in Fig. S2, Supporting Information). As a result, the timing error of the data acquisition was 0.4 ms in the worst case, and 0.03 ms in the typical case (Fig. S3). If we limit the scanning rate to lower than 1.0 V/s, then the error in the electrochemical potential caused by the time fluctuation would be below 0.4 mV. This is well below the resolution of the D/A converter (2.4 mV = (4.21 – (–5.54)) V/4096).

Evaluation of the Potentiostat

Three experiments were performed to evaluate the capability of the potentiostat: (1) examination of the linear response, (2) cyclic voltammetry, and (3) bulk electrolysis with coulometry.

To examine the linear response, an ohmic current passing a known resistor was measured with the potential scanning in the range of –4.0 to +4.0 V (details are described in Fig. S4 and its caption, Supporting Information). Typical results are shown in Fig. 5. The responses showed very good linearity, with the correlation coefficients greater than 0.9999. The maximum deviation from the linearity was ±2 μA, namely 0.2% of the full range. This is a sufficient specification for educational purposes and routine electrochemical experiments.

Other results are compiled in Fig. S5 (Supporting Information). One thing to note is that the linearity was suddenly lost when the current exceeded ±25 mA (Fig. S5, part a). This is due to the limitation of driving power of the operational amplifier, as described above. It is also worth noting that, even in this case, good linearity was kept in the range of –20 to +20 mA.

Cyclic voltammetry measurements were carried out on an aqueous ferrocyanide solution (Fig. 6), and the correlation between the peak current and the scan rate was examined as described in Meloni’s report. In all cases, a clean reversible voltammogram was observed. The observed half-wave potential was +0.243 V vs. Ag/AgCl, or +0.465 V vs. NHE. A linear fit of $i_p$ versus $v^{1/2}$ gave a slope of $(2.57 \pm 0.03) \times 10^{-4} \text{A} \cdot \text{s}^{1/2} \cdot \text{V}^{-1/2}$, from which a diffusion coefficient $D = (5.91 \pm 0.09) \times 10^{-6} \text{cm}^2/\text{s}$ was obtained. This is in good agreement with the literature value (6.5 $\pm 10^{-6} \text{cm}^2/\text{s}$).

Bulk electrolysis with coulometry was performed (Fig. 7) with an aqueous CuSO$_4$ solution (0.5 mol/L) and two copper plates (10 $\times$ 45 $\times$ 0.5 mm). The CE and RE terminals of the potentiostat were connected to the anodic plate, and the WE terminal to the cathodic plate. With the constant potential at –0.20 V, a cathodic current of –10 to –12 mA was observed. After 30000 s, the integrated current gave 434.8 C of the passed charge. The weight gain of the cathode and loss of the anode were +0.144 and –0.142 g, respectively, which are in good agreement with the theoretical value (0.143 g) calculated from the passed charge.

Discussion

The parts list with estimated cost is provided in Supporting Information (Table S1). The total cost is below 15000 JPY. This is much lower than standard electrochemical instruments for research, which typically cost 100000 to 1000000 JPY.
However, we should note that the potentiostat reported here has limited capability in comparison to the more expensive commercial instruments. Nevertheless, the present instrument has its own advantages when such high performance is not necessary.

There are other reports of low-cost electrochemical equipment. Rowe et al. reported “CheapStat,” an open-source “do-it-yourself” potentiostat. This instrument and related ones are commercially available at low cost (135 to 250 USD). The main concept of CheapStat is to use a microcontroller (ATX Mega from Microchip Technology) with 10-bit internal A/D and D/A converters. Such a design is advantageous in suppressing cost, because the external A/D and D/A parts are not necessary. There are also other reports of low-cost potentiostats based on similar microcontrollers. However, these microcontrollers are not powerful enough to present a decent user interface. Consequently, these microcontroller-based potentiostats require external PCs to carry out electrochemical experiments. On the other hand, the instrument reported here has a potentiostat and computer in one box, at a cost only slightly higher than the microcontroller-based instrument.

There is still some room for improvement in the present instrument. The most significant issue is the noise in the applied voltage and measured current. Although it is sufficiently low for many applications (0.2% of full scale, or 60 nA when full scale is 10 μA), it would be better if we can further suppress the noise. Presently, we implement the circuits on universal boards with hand soldering, and the geometry of the electronic parts is not optimized. Careful design of the printed circuit boards will help reduce the noise. Additionally, introduction of analog filter circuits and/or numeric filter on software may be an option. According to the report of Arévalo-Ramírez et al., on a low-cost potentiostat, introduction of the analog filter circuits (fifth-order Bessel and low pass) and the Kalman software filter were effective in reducing the noise. In the present instrument, implementation of the software filter is particularly easy, because the controlling software is based on a script language (LuaJIT) and can be easily replaced. This will be a subject of further investigation.

In summary, we successfully built a low-cost, standalone electrochemical instrument from a credit card-sized computer and inexpensive A/D and D/A converter chips. The instrument is capable of basic electrochemical measurements such as cyclic voltammetry and constant potential electrolysis, and should be useful for education and routine electrochemical experiments.

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Supporting Information

The programming details of the data acquisition (Figs. S1 and S2), evaluation of the data acquisition timings (Fig. S3), description of the linear response examination (Figs. S4 and S5) and the parts list with estimated cost (Table S1). This material is available free of charge on the web at http://www.jsac.or.jp/analsci. The LuaJIT and C source programs for the Raspberry Pi can be obtained at https://github.com/toshinagata/echempi/.

References

1. H. Katano, Rev. Polarogr., 2012, 58, 13.
2. H. Katano, Rev. Polarogr., 2012, 58, 23.
3. H. Katano, Rev. Polarogr., 2012, 58, 83.
4. H. Katano, Rev. Polarogr., 2012, 58, 89.
5. G. N. Meloni, J. Chem. Educ., 2016, 93, 1320.
6. “Products—Raspberry Pi”, https://www.raspberrypi.org/products/, retrieved on Jan 30, 2018.
7. An affordable ±12 V module is provided by Strawberry Linux Co., Ltd. (Part number 12039).
8. “3.2inch RPi LCD (B)”, http://www.waveshare.com/wiki/3.2inch_RPi_LCD_(B), retrieved on Jan 30, 2018.
9. “LuaJIT”, http://luajit.org/luajit.html, retrieved on Jan 30, 2018.
10. R. Ierusalimschy, “Programming in Lua”, 2nd ed., 2006, Lua.Org., Japanese translation, 2009, K. Shinjo, ASCII Media Works, Tokyo.
11. Since the oxidation potential of ferrocyanide depends strongly on the concentration and ionic strength, we do not compare this result with the literature values. See: I. M. Kolthoff and W. J. Tomesicek, J. Phys. Chem., 1935, 39, 945.
12. In Ref. 5, Meloni reported voltammograms showing $E_{1/2} = –0.25 \text{ V vs. Ag/AgCl}$, which is probably an error.
13. A. J. Bard and L. R. Faulkner, “Electrochemical Methods; Fundamentals and Applications”, 2001, Wiley and Sons, New York, 813.
14. A. A. Rowe, A. J. Bonjams, R. J. White, M. P. Zimmer, R. J. Yadgar, T. M. Hobza, J. W. Honea, I. Ben-Yaacov, and K. W. Plaxco, PLoS ONE, 2011, 6, e23783.
15. “IORodeo”, https://iorodeo.com/, retrieved on May 22, 2018.
16. “Low Cost Potentiostat: Criteria and Considerations for Its Design and Construction”, T. Arévalo-Ramírez, C. C. Torres, A. C. Rosero, and P. Espinoza-Montero, 2016 IEEE ANDESCON, Arequipa, 2016, 1 – 4.
17. A. Muid, M. Djamal, and R. Wirawan, AIP Conf. Proc., 2014, 1589, 124.