

Computer-Controlled Voltage/Current Source and Response Monitoring System for Electrochemical Investigations

Zoran Stevic¹, Misa Stevic², Ilija Radovanovic³, Predrag Stolic⁴, Milos Milesevic⁵, Milos Marjanovic⁶, Milan Radivojević⁷, Sanja Petronic⁸

¹ University of Belgrade, Technical faculty Bor, School of Electrical Engineering;

² Elsys, Belgrade

³ School of Electrical Engineering, University of Belgrade, Innovation Center of School of Electrical Engineering in Belgrade, Serbia

⁴ University of Belgrade, Technical Faculty Bor

⁵ School of Electrical Engineering, University of Belgrade

⁶ MS Kablovi, Paracin, Serbia

⁷ Mining and Metallurgy Institute Bor, Bor, Serbia

⁸ The Academy of Applied Technical Studies Belgrade, Katarine Ambrozic 3, Belgrade, Serbia

*E-mail: zstevic@tfbor.bg.ac.rs

Received: 28 January 2020 / Accepted: 26 March 2021 / Published: 30 April 2021

In this paper, a computer-controlled voltage and current source, together with a response monitoring system for electrochemical investigations, is presented. The measuring system consisted of two major parts: the measuring hardware (HW) and the proprietary software. The hardware included the data acquisition USB card NI USB 6211 from National Instruments Company as well as all needed circuits (the analogue front end, the signal conditioning circuits, and power supplies). The software is based on the LabVIEW platform from National Instruments, and it is designed to control the signal generation and measurements, to cancel the noise in the signals, and to calibrate the device. The supported electrochemical methods are potential, potentiostatic and galvanostatic measurements, as well as the cyclic voltammetry and impedance measurements. The system was thoroughly tested, and it was determined that the system characteristics fulfil the requirements for most of the electrochemical and bioelectrochemical measurements, supercapacitor characteristics investigations, and much more. The overall system is modular; the HW and SW can easily be upgraded to support different methods and purposes and, therefore, the performance of the system.

Keywords: electrochemical instrumentation, LabVIEW, computer-controlled voltage/current source, computer measurement, Electrochemical Impedance Spectroscopy

1. INTRODUCTION

In the last decade, the number of different systems based on electrochemical solutions, such as accumulator batteries, capacitors, and supercapacitors, together with various sensors has grown [1–5]. For example, batteries are typical devices with low specific power and high specific energy, while conventional capacitors can have high specific power but low specific energy. Therefore, supercapacitors fulfil the wide area between accumulator batteries and conventional capacitors in terms of specific power and specific energy. However, these components have one thing in common: their constantly improving characteristics, such as recent Li–Po batteries have higher capacities than the batteries a decade ago, various low-cost sensors with high precision are invented, while sensors size is reduced and end response improved.

All the previously mentioned progress would not be possible without different electrochemical investigations based on various material testing methods, characteristics measurements, and response monitoring [6]. There are a number of standard methods for testing electrochemical systems, but these methods are very expensive and not affordable for users. In this paper, a simple and affordable computer-supported system that allows most standard testing methods will be presented.

The computer-controlled response monitoring system for electrochemical investigations with voltage and current sources is a universal, easily customisable device intended for various investigation and research purposes [7]. It can be used in physical electrochemistry, electrochemical corrosion, battery testing, fuel cell testing, solar cell testing, sensor development, and more [8,9]. The system is designed for electrochemical laboratories, institutes, and faculties, where it could be used instead of standard equipment, while maintaining the quality of the results and measurement accuracy.

The idea behind the assembly of this system is modularity. The main system components are physically separated and can easily be changed/replaced. As mentioned in the abstract, the supported methods by default are the potential measurements, potentiostatic and galvanostatic measurements, cyclic voltammetry and impedance measurements. Each method uses a different application, while every application is detached from each other and, therefore, can easily be adopted for any user-needed purpose. Additionally, it is also possible to develop custom applications or to customise existing applications. When it comes to the hardware part of the system, the concept is similar. The system consists of three major modules: the data acquisition module, the analogue front-end module, and the power supply unit (PSU). Each is physically separated from the other. Therefore, it is easier to upgrade the system in order to achieve even better properties, such as the input and output impedance of the voltage and current generators, frequency characteristics, and measurement accuracy, or to add more input measuring channels if needed [10–12].

2. HARDWARE

Today, computer-assisted platforms and similar design methods are often used for engineering, product development, and for creating end-user products. When it comes to laboratory experiments, computer-assisted platforms are widely used due to their modularity and, therefore, upgradeability. They

also offer a powerful computing performance platform with other capabilities, such as experimental simulations, which could be executed either in the laboratory or remotely over the Internet connection [13,14].

Instead of classical measurement equipment, general purpose personal computers, inexpensive acquisition card and related software are increasingly being used. When combined with an application-specific user interface, a system suitable for collecting, measuring and processing data and controlling various experiments can easily be achieved [15]. These systems can be adapted for various purposes and user needs, from low-cost systems to high performance ones, while high precision, sampling rate, and accuracy can be achieved.

A system for control and measurement based on a PC and external interface for monitoring the response of the electrochemical system and signal generation was developed. The external interface is compatible with any Microsoft Windows® 7 or newer based PC with USB2.0 or higher interface. The USB connector is used for data transfer, while the separate AC plug is used to power the device and, therefore, to ensure that no additional PC requirements or other devices are needed for operation.

In order to meet the requirements of the control and measurement system, the circuit was designed with the characteristics shown in Table 1, and the principal scheme is shown in Fig. 1.

Table 1. Electrical characteristics of the system.

Number of voltage outputs	1
Number of current outputs	1
Voltage output range	± 10 V
Maximum output current	500 mA
Voltage/current output resolution	± 0.15 μ V/ ± 10 pA
Number of voltage inputs	2
Input voltage ranges	± 0.2 V, ± 1 V, ± 5 V, ± 10 V
Voltage input accuracy	± 3 μ V
Input impedance	10^{10} Ω
Sampling rate	250 kS/s

The hardware part of the system is divided in three major parts:

- Data acquisition module
- Analog front-end module
- Power supply unit

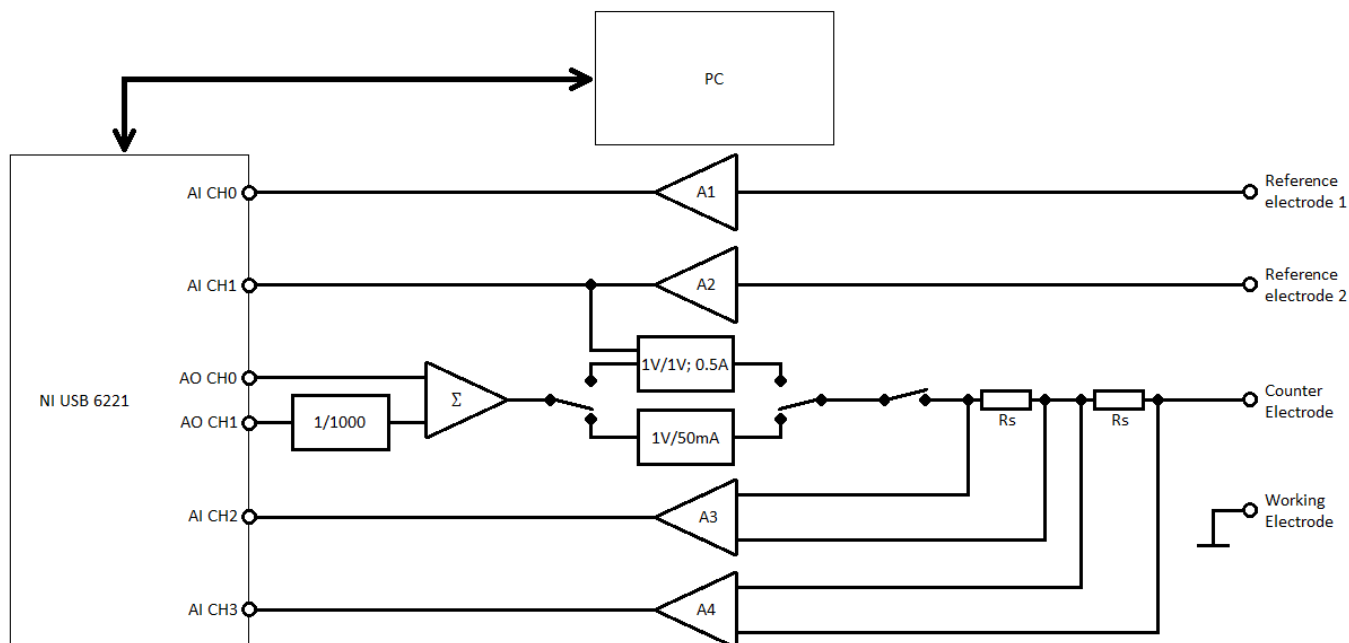


Figure 1. The principal scheme of the system.

2.1 Data acquisition module

For the measurement and system control, a commercially available data acquisition card was used: NI USB-6211 (the USB multifunction input/output device from National Instruments company). Compared to other successors in the same price range, it has a fairly high performance. It is a complete solution for a user-configurable data acquisition device, offering analogue and digital inputs and outputs and two 32-bit counters. It also has integrated high-speed variable gain amplifiers on analogue input channels so that users can set the input range on each channel individually. All these features make it a very useful solution for various applications, including the control and design of laboratory equipment and instruments, academic research, data logging, in-vehicle data acquisition, and more [16]. Having portability in mind, the device is completely controlled and powered over the USB interface.

Table 2. Specifications and features of the NI USB 6211 acquisition card.

Number of input analogue channels (AI)	16 (single ended)/8 (differential)
Number of output analogue channels (AO)	2
Number of input digital channels (DI)	4
Number of output digital channels (DO)	4
Sampling rate	250 kS/s (multiplexed)
I/O voltage ranges	±0.2 V, ±1 V, ±5 V, ±10 V
AD convertor resolution	16 bit
DA convertor resolution	16 bit

The generation of voltage and current signals, the processing of analogue signals coming from the sensing electrodes, and the monitoring of the system's response to these signals was processed by a previously mentioned data acquisition card. The most important features of the NI USB-6211 are shown in Table 2.

2.2 Analog front-end module

The generation of voltage and current output signals, as well as the monitoring of the system's response to these signals is performed through a set of electronic circuits, which forms the analogue front end (AFE). The input signals from reference electrodes 1 and 2 are buffered with amplifiers A1 and A2 and sent to the acquisition module (Fig. 2). Consequently, high input impedance of the system is achieved, and, therefore, the stability of the system is improved due to the fact that the electrodes by themselves can have a large internal resistance.

The analogue voltage outputs from the acquisition module (AO CH0 and AO CH1) can both be used simultaneously, depending on the user requirements. However, there is a difference in system behaviour depending on the analogue output used. The voltage from output AO CH1 is divided by 1000 and then sent to the summing amplifier, while the voltage from output AO CH0 is sent directly. That means that the output AO CH1 can generate the output signals within a ± 10 mV range on the output of the summing amplifier. Following the previous, the signal is brought to a series of relays (Re1, Re2), whose purpose is to switch between the potentiostat or galvanostat used for the system output signal generation. The potentiostat (U6=OPA548 in Fig. 2) amplifies the output voltage from the summing amplifier by 1, and, therefore, the maximum output voltage of the whole system is ± 10 V. However, its maximum output current is 500 mA, which is far higher than the outputs from the DA converter or any other internal amplifiers. The galvanostat (U7=OPA548 in Fig. 2), on the other hand, has a ratio of 1 V/50 mA, which means that the maximum output current is 500 mA in case that the control signal is at its maximum of 10 V. Knowing that the output AO CH1 is divided by 1000 before its summing with AO CH0, in potentiostatic mode, it can generate a system output voltage of up to ± 10 mV, while in the galvanostatic mode currents of up to 500 μ A can be generated. As already mentioned, both analogue outputs from the DA converter can be used simultaneously, so it is possible to keep both the voltage output range of AO CH0 (± 10 V) and the resolution of the AO CH1 on the same output channel from the system (counter electrode). In potentiostat mode, the absolute maximum resolution is $10 \text{ mV}/2^{16}=0.15 \text{ } \mu\text{V}$, while in galvanostatic mode it is $0.5 \text{ mA}/2^{16}=7.63 \text{ pA}$. However, due to component tolerances, various environmental effects on the system, signal noises, etc. in the electrical characteristics of the system (shown in Table 1), the resolution of the AO CH0 DA converter output is chosen. The overall system design with the features described above is the original design and the authors' own creation. In Fig. 2, the analogue front-end circuit diagram is shown.

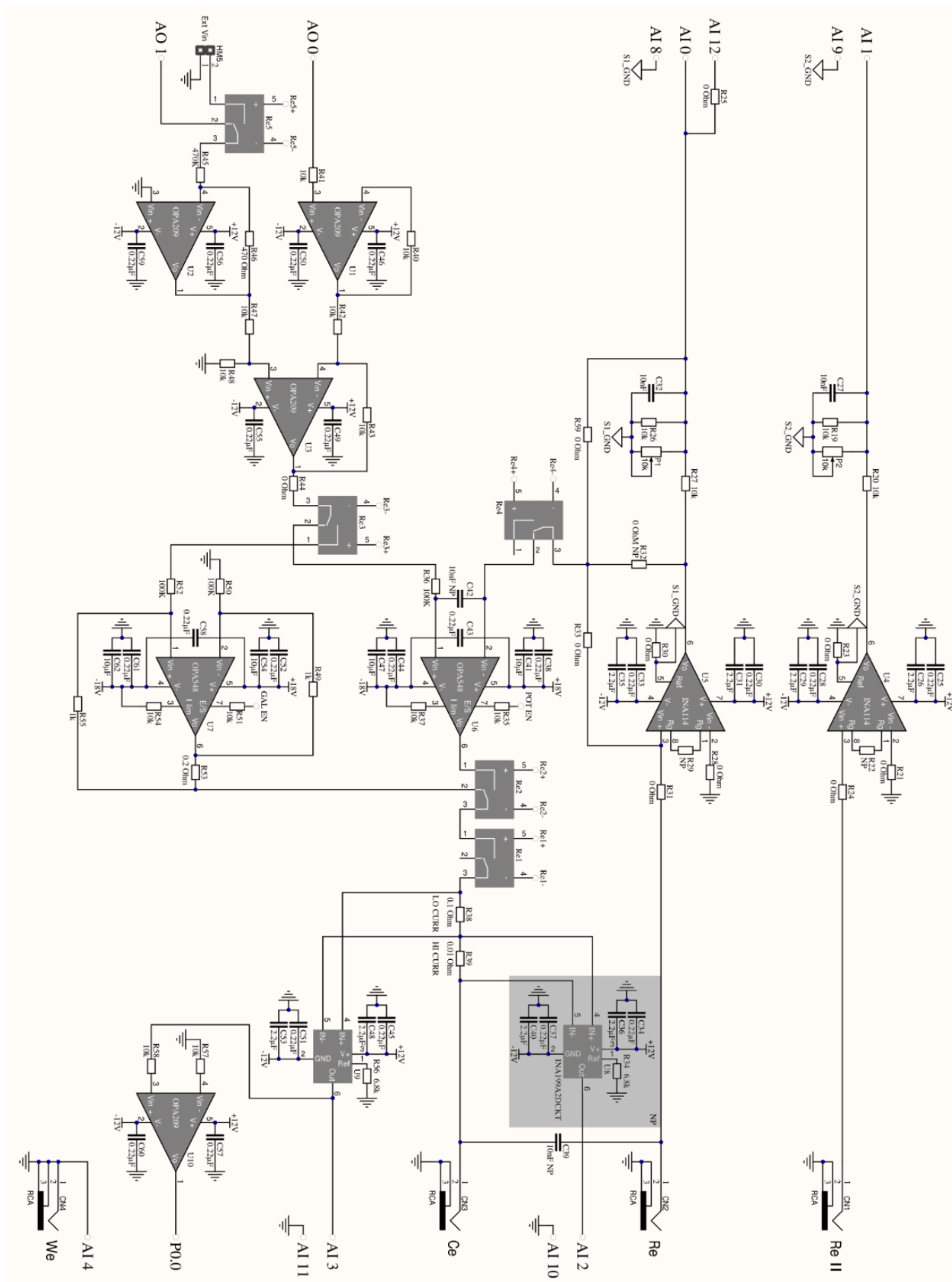


Figure 2. The schematic diagram of the analogue front-end module.

2.3 Power supply unit

The power supply unit consists of two separate switched-mode-based 220 V AC input and 18 V DC output modules. The main reason for using the switched-mode power supply is due to its advantages: high efficiency (>80%), small size, high output current (maximum of 3A), compact design, and light weight. However, there are well-known disadvantages of the switched-mode-based power supplies: output voltage ripple, glitches, and spikes. On the other hand, all three mentioned disadvantages require a single solution: solid output voltage filtering. Having that in mind, the analogue front-end module has the on-board power supply filtering section, which greatly reduces the noise from the power supply. Besides that, for powering the measurement amplifiers and other sensitive parts of the system, the voltage regulator circuits are used to ensure a clean and stable power supply.

3. SOFTWARE

The software platform used for this particular system is LabVIEW (from National Instruments company) due to its high standard in the area of modern virtual instruments [17,18]. LabVIEW is based on the principles of virtual instruments with a graphical user interface. The graphical user interface has two windows: the front panel and the block diagram.

LabVIEW is an object-oriented, graphical programming language. Therefore, the user interface is built using a set of various tools and objects. The user interface is known as the front panel. The code is then added by using graphical representations of functions to control the front panel objects, shown on the block diagram. In this paper, the front panels, as well as block diagrams, are shown below for the most common electrochemical methods.

For external connections over the AD-DA converter, the NI data acquisition driver collection is used. The installation of these packages and the AD-DA converter results in a powerful development and measurement system that can be used for system control and signal processing.

Applications have been made for various electrochemical investigation methods. The potentiostatic and galvanostatic methods, as well as cyclic voltammetry, are presented in this paper. Every application consists of a unique block diagram and front panel, making them user friendly. Therefore, choosing between different methods is done by running the appropriate application. In that way, it is ensured that no access code is present and that the system is well optimised and running stable. Besides that, the front panels are made in a minimalistic style, so that user can quickly set all needed parameters and monitor the results. In addition to the possibility of continuous monitoring of the flow of the process, it is also possible to continuously record data in the appropriate file on the computer. The data is recorded as raw measurement values in time, and the specified file are saved in TXT format, which allows the obtained data to be further processed (DSP, Data Science, etc.) and interpreted by any external data visualisation and analysis software. This feature enables the existing system to be integrated into other systems and to achieve certain compatibility between them.

3.1 Galvanostatic method

The galvanostatic method refers to an experimental technique whereby the working electrode is used as an output of the system, maintaining a constant current in the electrolyte used in the experiment. In galvanostatic tests, the potential of the reference electrode is plotted in a potential versus time diagram at constant current. This technique is most widely used to measure corrosion rate and electrochemical reactions. It is used for controlled bi-directional polarisation of metal surfaces in electrolytes in order to observe cathodic and anodic behaviours.

The voltage levels on the AI CH0 and AI CH1 channels of the acquisition card were processed (Fig. 2). After filtering and averaging, the potential value (η [V]) was obtained, which represents the galvanostatic response, and is displayed on the η [V] indicator and on the time diagram.

The current intensity is achieved by the voltage-controlled current generator, which is included in AFE. The control voltage is set by the DAQ assistant block in relation to 1 V/50 mA. The length of the galvanostatic impulse is controlled by setting the t_p [s] since the application compares the wanted impulse length with the current time and then defines the end of the impulse. Similar to the pulse length, all the other parameters can be set in the front panel of the application: output current I [mA], beginning potential E_{beg} [V], the duration of the impulse t_p [s], t_p [min] and t_p [h], and pause time, t_0 , which is also given in the format of seconds, minutes, and hours. Besides the control boxes, the control panel also contains the indicators of the actual current, and the overvoltage and time have been shown on the panel as well as the $E=f(t)$ graph, which can later be saved as an image in PNG format.

The wanted measurement record file name and path are chosen right after starting the application. That way, the application is capable of recording the measurements in the file in real time so that in the case of any system or experiment failure (i.e., power outage), all the data recorded up to that very moment is saved.

3.2 Polarization curves

By recording the family of galvanostatic curves for different current densities and reading the corresponding overvoltage, a set of points for the polarisation curve was obtained. The current is introduced in a logarithmic scale in order to linearise the curve in the Tafel region. At the point of intersection of the tangents to the anodic and cathodic polarisation curves, a corrosion current is obtained.

3.3 Potentiostatic method

In the potentiostatic method, similarly as in the galvanostatic method, the pulse is first defined. Afterwards, the user sets the t_p [s], the total time of the experiment (period) t_u [s], and the condition for stopping the time loop. As is usual with all voltage methods, the current reading is performed, using AI CH2 and AI CH3 in this case, depending on the wanted range and resolution, and the assigned voltage is on the zero-output channel AO0 (Fig. 2).

3.4. Cyclic voltammetry

In this method, current measurements were made using the channels AI CH2 and AI CH3, while channels AO CH0 and AO CH1 were used for setting the output voltage (Fig. 2), as in the potentiostatic method. The current measurement and assignment of the output voltage (channel AO CH0 and AO CH1) were the same with the potentiostatic method, but the output voltage was variable over time. Therefore, the user has to set the following: the beginning value of the output potential (E_{beg}), the final potential (E_{fin}), and the potential sweep rate (dE/dt). All these settings are available on the front panel of the application, known as the control boxes.

The output voltage and the current reading resolutions also remain the same as in the potentiostatic method. However, because of the nature of the method, requiring constant changing of the output voltage, the different, slightly more complex application is needed. The main difference in comparison with the potentiostatic method application is that the cyclic voltammetry application calculates the desired output voltage in real time, while executing the cycle, according to the following equations:

$$E = k \cdot t + E_{beg}; t \leq t_1$$

$$E = -k \cdot t + 2E_{max} - E_{min}; t > t_1$$

where E is the actual potential, t is time, k is the sweep rate, t_1 is the rise time, E_{beg} is the beginning potential, E_{max} is the maximum potential, and E_{min} is the minimum potential.

4. RESULTS AND DISCUSSION

A prototype of the developed system and parameter adjustments were made. Using the 5½ digit voltmeter PRIMA B7-21A, EAST TESTER LCR METER ET 4410, and lock-in laboratory multi-meter KEITHLEY 193A SYSTEM DMM, the measurement system was calibrated for the selected range. Then, the complete system was tested and tuned using the accompanying software. Setting the offset and gain constants was reduced to the input constants of the LabVIEW application. The measurement errors were less than 0.1% in all ranges.

Signal-to-noise ratio measurements of the system were also performed. The system was thoroughly tested under various conditions using RTB 2002, which is a premium 2-channel oscilloscope from Rohde & Schwarz, with the accompanying software, R&S Application Bundle RTB-PK1.

There are several commercial instruments that can be purchased on the market, but their prices are much higher, and their characteristics are either slightly better or slightly weaker [19]. A comparison with a popular Gamry instrument with similar characteristics is made here. The results obtained using this measurement system are compared with those obtained in the same electrochemical conditions using the commercial galvanostat-potentiostat Gamry Interface 1010E [20] as the reference instrument. A

series of experiments and comparative analyses [21–23] were executed, and the representative results obtained by the different methods of the electrochemical tests are presented here.

4.1 Galvanostatic method

Experimental diagrams for a carbon electrode in a 1 M aqueous solution of sodium nitrate (NaNO_3) at an amperage of 100 mA/g and a pulse duration of 800 s are shown in Fig. 3. Activated carbon (Aktivkohle, MERCK) was used as a basic active material, and polyvinylidene difluoride (PVDF) was used as a binder [2,24,25]. The diagrams obtained by the reference instrument, Gamry Interface 1010E, and the tested system are presented. The maximum deviation was below 0.5%, which is within the allowed limits, and this can be caused by a change in laboratory conditions.

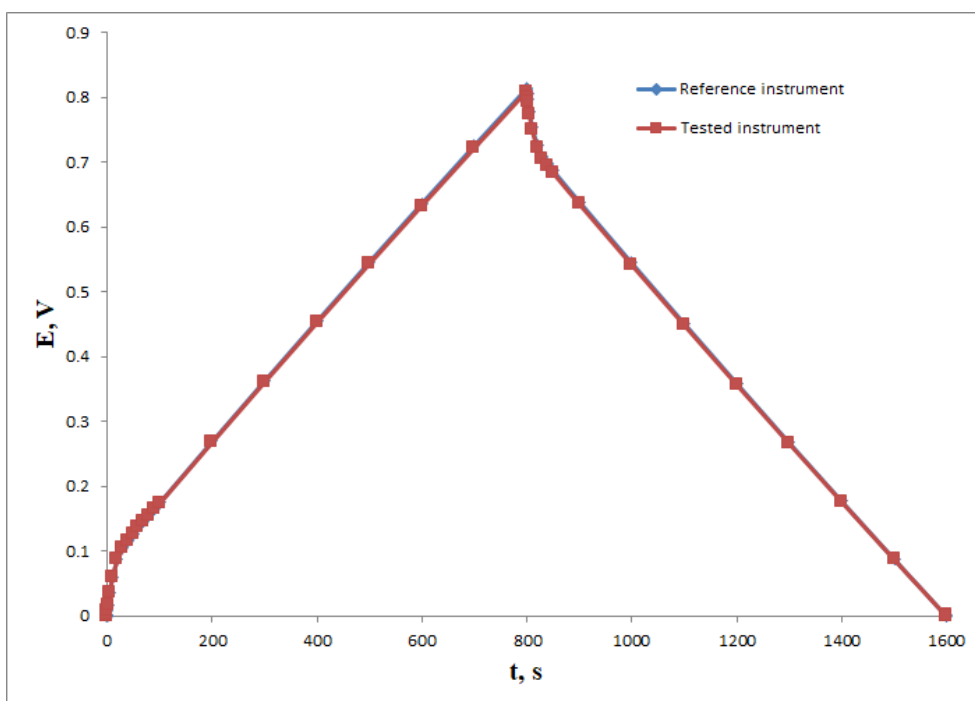


Figure 3. Galvanostatic diagrams obtained by the reference instrument and the tested measurement system.

4.2 Polarization curves

Polarisation curves for mild steel 0345 recorded in an aqueous 1 M NaCl solution by the reference instrument, Gamry Interface 1010E, and the tested system are shown in Fig. 4. The maximum deviation was below 0.4%, which is within the allowed limits.

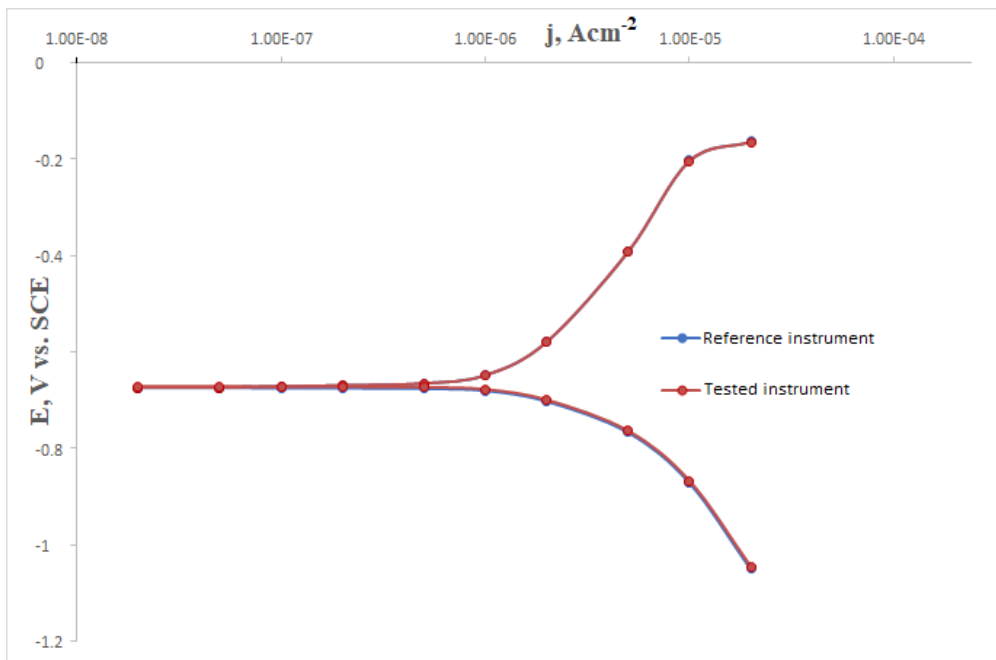


Figure 4. Polarization curves obtained by the reference instrument and the tested measurement system.

4.3 Cyclic voltammetry

Cyclic voltammograms for a carbon electrode in a 1 M aqueous solution of sodium nitrate (NaNO_3) at the overpotential changes speed of 2 mV/s are shown in Fig. 5. Activated carbon was used as the basic active material PVDF. The obtained results showed that no major difference in test results were present between the two systems that were used.

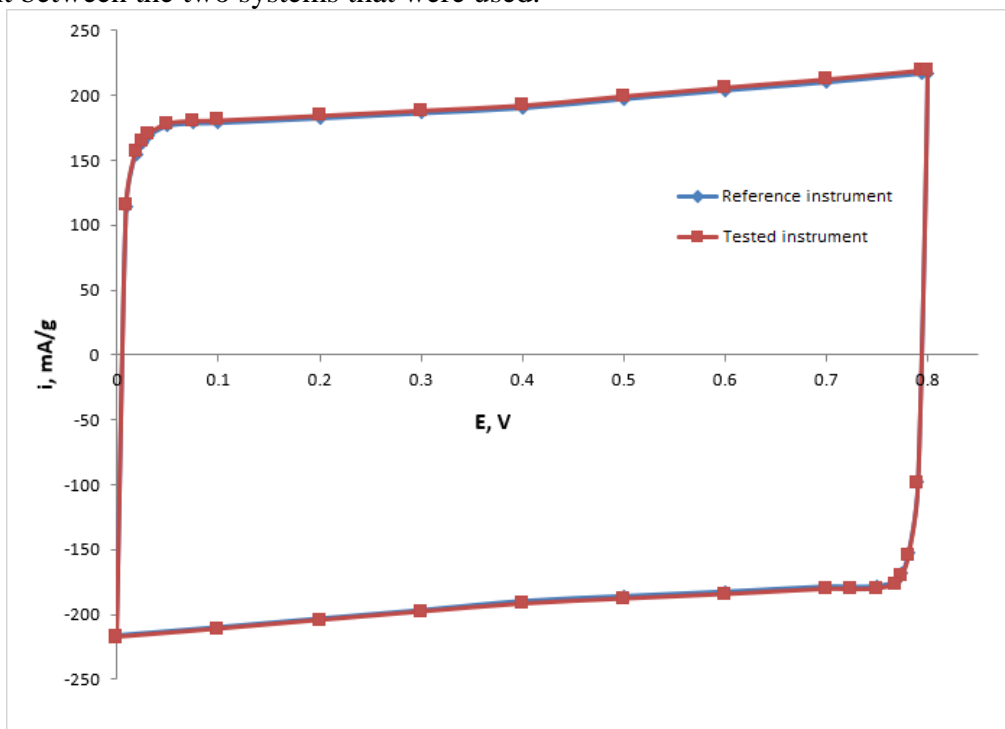


Figure 5. Cyclic voltammograms obtained by the reference instrument and the tested measurement system.

4.4 Potentiostatic method

A time diagram of the responsive current for the carbon electrode in a 1 M aqueous solution of sodium nitrate (NaNO_3) at a potentiostatic pulse with an intensity of 100 mV and a duration of 500 s is shown in Fig. 6. The maximum deviation was below 0.4%, which is within the allowed limits.

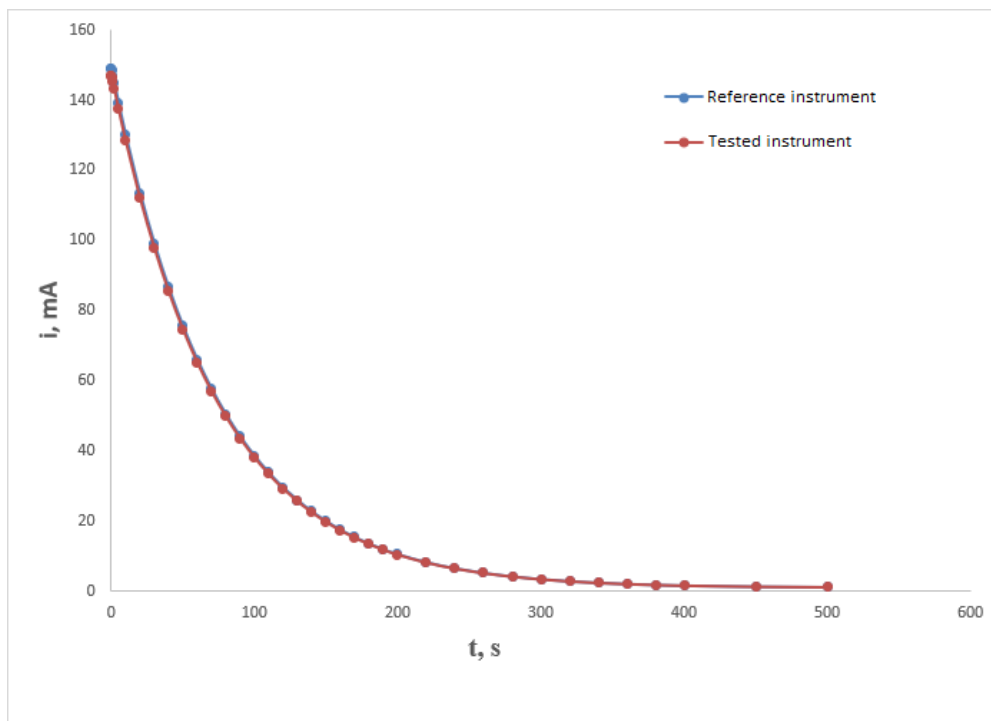


Figure 6. Potentiostatic diagrams obtained by the reference instrument and the tested measurement system.

The measurement system tests show that all expectations were fulfilled and that the basis for further improvements (WEB and CLOUD laboratory, IoT technology, etc.) was founded.

5. CONCLUSION

The default version of the system was thoroughly tested in many different conditions with material samples, and the obtained results were compared with test results of referent commercial devices. The obtained results proved that it is possible to match the most significant characteristics of more expensive devices for most of the investigation methods using the presented low-cost device.

The appropriate hardware (data acquisition device with desired external analogue front end) in conjunction with a personal computer equipped with the software developed in the LabVIEW environment is a very powerful, customisable measurement system applicable in scientific and research fields. Due to its characteristics, it can be adopted to meet low-cost requirements or, on the other hand, to serve as a more expensive but faster and more precise device. Thanks to its open architecture, it can

successfully replace a large number of specialised and very often high-cost measurement equipment. The presented system can be further used in new areas and scientific fields, as well as developed by adding new methods and virtual instruments. Currently, this measurement system is in use in electronics, electrical engineering, and physics for educational purposes. It could easily be adapted for chemistry and physical chemistry.

Since the system is the author's own creation and since the hardware and software are fully customisable, in further developments the system could be adapted for remote operation and data sharing among users, which would increase the usability of the described system. Besides the ability to record the results in a suitable file, cloud support is also considered as a very powerful potential upgrade to the existing system.

ACKNOWLEDGEMENTS

This research was funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia, with contract numbers 451-03-9/2020-14/200131 and 451-03-68/2020-14/200223.

References

1. H. Deng, M. Zhu, T. Jin, C. Cheng, J. Zheng and Y. Qian, *Int. J. Electrochem. Sci.*, 15 (2020) 16
2. S. Martinović, M. Vlahović, E. Ponomaryova, I. V. Ryzhkov, M. Jovanović, T. Volkov Husović and Z. Stević, *Int. J. Electrochem. Sci.*, 12 (2017) 7287
3. C. Liu and Z. Zhang, *Electrochemical Materials Design for Micro-Supercapacitors In Supercapacitor Design and Applications*, Editor Zoran Stević, Intech, (2016) Rijeka, Croatia.
4. Z. Yunusa, M. N. Hamidon, A. Kaiser and Z. Awang, *Sensors & Transducers*, 4 (2014) 61.
5. J. Grimshaw, *Electrochemical Reactions and Mechanisms in Organic Chemistry*, Elsevier, (2000) Amsterdam, Netherlands.
6. Z. Stević, Z. Andjelković and D. Antić, *Sensors*, 8 (2008) 1819.
7. B. Paton, *Introduction to NI ELVIS*, National Instruments Corporation, (2009) Austin, Texas.
8. Z. Stevic, M. Rajcic-Vujasinovic and I. Radovanovic, *Int. J. Electrochem. Sci.*, 9 (2014) 7110.
9. Z. Stević, M. Rajčić Vujasinović and A. Dekanski, *Sensors*, 9 (2009) 7365.
10. G. Saggio, *Principles of Analog Electronics*, CRC Press, (2014) Boca Raton, Florida.
11. P. Purkait, B. Biswas, S. Das and C. Koley, *Electrical and Electronics Measurements and Instrumentation*, McGraw Hill Education India Private Limited, (2013) New Delhi, India.
12. D. F. A. Edwards, *Electronic Measurement Techniques*, 2nd ed.; Butterworth-Heinemann, (1991) Oxford, United Kingdom.
13. J. Yun, I. Y. Ahn, J. S. Song and J. Kim, *Sensors*, 19 (2019) 4567.
14. S. K. Yadav, S. Raj and S. S. Roy, *Int. J. Adv. in R&T*, 2 (2013) 1025.
15. K. Rojek, R. Schmechel and N. Benson, *Meas. Sci. Technol.*, 31 (2020) 015901.
16. National Instruments Team, *NI USB-621x User Manual*, National Instruments Corporation, (2009) Austin, Texas.
17. National Instruments Team, *Getting Started with LabVIEW*, National Instruments Corporation, (2013) Austin, Texas.
18. S. Folea, *LabVIEW - practical applications and solutions*, Intech, (2011) Rijeka, Croatia.
19. T. Dobbelaere, P. M. Vereecken and C. Detavernier, *HardwareX*, 2 (2017) 34.
20. Gamry Instruments, *Manual2*, <https://www.gamry.com/assets/Uploads/Interface-1000-Operators-Manual2.pdf>
21. Gamry Instruments, *Echem Analyst™ software*, <https://www.gamry.com/assets/Uploads/Echem-Analyst-QSG-988-00016-rev-2-for-web.pdf>

22. M. Smiljanić, Z. Rakočević and S. Štrbac, *Int. J. Electrochem. Sci.*, 8 (2013) 4941.
23. M.D. M. Dryden and A. R. Wheeler, *PLOS One*, 10 (2015) e0140349.
24. Q. Abbas, D. Pajak, E. Frackowiak and F. Béguin, *Electrochim. Acta*, 140 (2014) 132.
25. Z. Zhu, S. Tang, J. Yuan, X. Qin, Y. Deng, R. Qu and G.M. Haarberg, *Int. J. Electrochem. Sci.*, 11 (2016) 8270.

© 2021 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).