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Transistor Amplifier as an Electrochemical Transducer with Intuitive Optical Read-out: Improving Its Performance with Simple Electronic Solutions

Karel Lacina[a,*], Jaromír Žák[b], Jakub Sopoušek[a], Zoltán Szabó[c], Tomáš Václavek[d,e], Jiří Žeravík[e], Pavel Fiala[c], Petr Skládal[a,e]

[a] *CEITEC – Central European Institute of Technology, Masaryk University, Kamenice 5, Brno, 625 00, Czech Republic*
[b] *Department of Microelectronics, Faculty of Electrical Engineering and Communication, Brno University of Technology, Technicka 3058/10, 616 00 Brno, Czech Republic*
[c] *Department of Theoretical and Experimental Electrical Engineering, Faculty of Electrical Engineering and Communication, Brno University of Technology, Technicka 3058/10, 616 00 Brno, Czech Republic*
[d] *Institute of Analytical Chemistry of the Czech Academy of Sciences (UIACH), Veveří 97, Brno, 602 00, Czech Republic*
[e] *Department of Biochemistry, Faculty of Science, Masaryk University, Kamenice 5, Brno, 625 00, Czech Republic*

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ABSTRACT

A platform for electrochemical transduction suitable for miniaturised point-of-care diagnostic solutions with intuitive optical read-out was designed. Electrolytic current from electrochemical cell was transduced into the glow of a light-emitting diode. Its performance was optimised and several variants of transducing circuitry were tested. The circuit comprising field-effect transistor (FET) exhibited the sought abilities – absolute simplicity and high and tuneable sensitivity of the transducing device. Limit-of-detection, *i.e.* a signal readable by naked-eye without any additional instrumentation was as low as 4 μM for direct assay of H_2O_2. The whole transducing system employing FET consisted of 4 off-the-shelf components and its price reached <0.3 € even at small-scale experimental production. As our system was rather suitable for the semiquantitative "YES/NO" applications due to the steep response curve, an alternative circuitry for widening the linear range was also probed. Finally, rather higher initial voltage that was required in the electrochemical cell for FET-based transducer lead us to design a further simplified and more variable circuit employing the operational amplifier.

1. Introduction

Two popular terms of current sensing science – point-of-care (POC) and lab-on-chip entail and demand miniaturisation, simple operation, direct and straightforward interpretation of results and also disposability of the sensing part upon manipulation with infectious materials [1]. Simple (thus robust) and cheap detection schemes are therefore desirable. The most simple and natural method of signal registering is human eye. The intuitive naked-eye detection [2] is widely used in the POC devices such as pregnancy tests working on the principles of lateral flow assay including paper microfluidics [3–5].

The electrochemical (bio)sensing predominantly utilise sophisticated instruments – potentiostats, for the precise and reproducible control of experimental conditions. However, the fully-controlled electrochemistry with the help of potentiostats is in some cases challenging – merging of miniaturisation and minimisation of costs for its performance.

Although there is a plethora of reports on electrochemical POC devices, only few attempts addressed the combination of sensitivity of electroanalytical techniques and simplicity of the naked-eye read-out (potentiostat-based approaches are not involved). For example, the presence of H_2S in the sample lowered resistance of the polyaniline layer which resulted in signalling by light emitting diode (LED) [6]. Furthermore, sophisticated paper-based microfluidic system for the detection of glucose exhibited also user-friendliness of the lateral flow tests. The integral metal/air battery powered both the electrochemical sensor and the electrochromic read-out [7].

Recently we have designed a simple five-component detection device consisting of two resistors, one LED, a bipolar transistor and

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[*] Corresponding author.
E-mail address: lacinak@chemi.muni.cz (K. Lacina).

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an electrochemical cell. An analyte-dependent current flowing through the cell was amplified by the bipolar transistor resulting in a glow of the light emitting diode [8]. The applicability of such simple electrochemical transducer with the optical read-out has been proved on the detection of glucose (using both redox reactions of enzymatically generated H_2O_2). The detection system worked on the basis of electrolytic cell, *i.e.* application of a particular voltage between two electrodes was followed by electrochemical reactions – reduction on the cathode and oxidation on the anode (analogously to biamperometric cell [9–11,10]).

To further optimise the performance of our system for future POC applications, several alternative constructions of electronic circuitry were tested in the present study. These included the amplification with unipolar field-effect transistor and usage of a circuitry that should improve the linear range due to stabilisation of the potential in the cell. Finally, the transduction with operational amplifier was probed as well.

It has to be said, that we do not want to compete with ordinary much more sensitive and well performing potentiostated analytical solutions, we rather focus on a design of functional, low-cost and simple analytical tools resembling disposable lateral flow tests with intuitive visual detection.

2. Experimental

Measuring circuitry was constructed using common electronic components from local suppliers (TME Electronic Components, Poland and GM Electronics, Czech Republic). 50 mM phosphate buffer (pH 7.4, in 100 mM KCl) and flow rate 150 µl/min were used for all electrochemical flow-through experiments. The 2-channel screen-printed electrode (two equal platinum disk electrodes on a ceramic wafer, 1 mm in diameter of electroactive surface, type AC2. W2.RS, BVT Technologies, Czech Republic) was inserted into a home-made flow-through cell [9] and used in the electrolytic setup [8]. Before each measurement, the electrodes were cleaned by immersion into concentrated chromosulfuric acid for several minutes, then polished using MicroCloth with alumina slurry (0.05 µm, Buehler) and thoroughly rinsed with deionised water.

Changes of potential in the electrochemical system as a response to injections of different concentrations of H_2O_2 (Penta, Czech Republic) into the flow-through cell were followed by Nano Volt/Micro Ohm Meter 34420A (Agilent) operated by in-house developed software LabTools (P. Skládal). Discrete values of potential were measured using Multimeter U1253A (Agilent). All other chemicals were of the highest purity available and used as received.

3. Results and Discussion

Initial notes:

a) If we assume that all analytical parameters of the assay are appropriate (limit of detection, sensitivity, repeatability, suitable difficulty of operation, turn-around time of the method *etc.*), the economic aspects become the only limiting factor for commercial acceptance. From the viewpoint of industrial production, the price and construction simplicity actually represent one and the same parameter of the developed assay. Consequently, the construction simplicity will be the main parameter considered throughout this report since the designed device is predominantly studied and evaluated for semiquantitative "YES/NO" applications. However, the emphasised simplicity is in the scope not only because of the commercial attractiveness – a cheap sensor can be disposed after each measurement which is key parameter upon handling with potentially infectious samples, and in the case of direct contact with blood when initial sterility of the sensing zone is also an important issue.
b) A transistor in common electronic circuits most often serves for an amplification of signal (either current or voltage). Herein, the transistor served rather for the analogue transduction of the electrolytic current into the glow of LED.

3.1. Limit of detection with FET

The previously developed platform for the transduction of electrochemical signal to a visual read-out was upgraded due to the employment of a field-effect transistor. It retained the simplicity of the previous solution with the bipolar transistor [8]; in addition, it provided much higher sensitivity.

The proposed system acquired unsurpassable abilities with the unipolar N-MOSFET transistor (IRLML6246) (Fig. 1A,B). Details of the function of the studied device and following principles were the same and can be found elsewhere [8,9]. Briefly, a voltage is applied on the electrochemical cell by means of a particular value of resistor R_1 upon the chosen supply voltage and only background currents are flowing through the cell. Such value of resistor R_2 is used that the transistor is initially closed and LED is not gleaming. In the case that redox active analyte, *e.g.* H_2O_2, enters the cell, electrochemical reactions occur, potential in the cell (E_{cell}) drops and current flows also through the voltage divider R_1 and R_2. The transistor is thus opened and LED starts to shine – the detection event occurs, *i.e.* response is registered (Fig. 1C). Analogous properties to our previous report [8], were observed also with this setup – a higher sensitivity with increasing R_1. The ratio of R_1 and R_2 resistances is given by the initial condition of darkened LED. The linear relation of $R_1 = 0.65^*R_2$ was determined at our experimental conditions. The limit of detection was 4 µM H_2O_2 when resistance of R_1 equals to 200 MΩ. This limit of detection is not given by the smallest detectable change of the potential in the electrochemical cell but rather by the smallest concentration of H_2O_2 which generates a glow of the signalling LED still visually recognisable by the naked eye.

The sensitivity of the device – the change of potential in the cell as a response for particular concentration of an analyte (*e.g.* 4 µM H_2O_2), increases with increasing R_1 (Fig. 1D,E). Similarly as in the case with the bipolar transistor, the theoretical sensitivity of the circuit employing the unipolar transistor is also limited by its physical properties, *i.e.* finite resistance of the gate electrode. To obtain theoretically infinite amplification is not possible because when R_1 and R_2 are comparable to the value of the resistance of the particular gate electrode, the current flowing through the gate is not negligibly small and will influence the function of the voltage divider. Moreover, the initial potential (baseline) decreases as well, which results in the limited usability of the high values of resistance.

Interestingly, the effect of capacitive currents was apparent – it was caused by the slow charging of the electrode double layer through big resistance of the voltage divider consisting of R_1 and R_2. Charging of the electrodes occurs slowly, thus limiting the utilisation of high-sensitive setups with high values of resistors in experiments where quick response is desired. This phenomenon is apparent for measurements with increasing R_1 values in the direction from black to red curves (Fig. 1D, $t > 20$ min) when only buffer was present in the cell after the highest tested concentration of H_2O_2. This seeming inconvenience could be advantageously utilised in sensing of non-faradaic processes including *e.g.* conducting of ionic Helmholtz double layers, flux of charged species, *etc.*