

Hybrid electrochemical – optical sensors with internal electrolysis

In this project we propose a new type of sensors utilizing the concept of “internal electrolysis”, i.e. occurring in the absence of external polarization. In this system the electrodes are connected by a metallic conductor (short circuit) and the driving force of the electrochemical spontaneous process is the difference of potentials of both electrodes. On one of the electrodes the reagent undergoes spontaneous oxidation, while on the second electrode, another reagent undergoes oxidation. This system can be regarded as an electrochemical cell with electrodes connected directly by a conductor. However, the purpose of this system is not to obtain electrical energy, we would like to use it for analytical purposes. In the proposed system on one electrode the analyte undergoes spontaneous oxidation or reduction, while the other short-circuiting electrode is undergoing complementary redox process leading to change of absorption or emission of the substance deposited on the electrode or present in the solution – an optical transducer (e.g. tungsten oxide, a redox or conducting polymer). In this system the charge consumed in the electrochemical reaction at one electrode is the same as that used at the second electrode. Because the absorbance (or fluorescence intensity) of an electrochromic substance is proportional to its amount, we expect that the optical signal (e.g. absorbance of the formed product) is proportional to the charge consumed in the electrochemical reaction of the analyte. In this project we would like to join advantages of electrochemical and optical sensors: a broad range of analytes and optimized analytical procedures typical for electrochemical sensors and simpler construction of optical sensors as well as appearance of a colorimetric/fluorimetric signal which can be simply detected.

The concept of the proposed system, its properties and possibilities will be tested starting from relatively simple model examples. We will study the properties of the system, where oxygen and hydrogen peroxide will serve as model analytes. They can undergo electrochemical reduction e.g. on platinum sensing electrode. A significant benefit of the new system, that can be achieved due to separation of receptor and transducer system, is avoiding direct and potentially deteriorating contact of the analyte with the electrochromic material (e.g. degradation of a conducting polymer upon contact with a strong oxidant). The redox reaction between the analyte and the electrochromic compound in this case occurs as two half-cell reactions on separate electrodes. In this way it is also possible to utilize catalytic properties of the electrode contacting with the analyte.

In the next step more advanced model systems will be studied, with enzymatic electrodes and ion-selective electrodes (ISE). In the first case, the electrochemical process at the enzymatic electrode (e.g. oxygen reduction in the presence of laccase) will induce absorption or emission changes at the other electrode. In case of ion-selective electrodes changes of their potential (accompanying change of analyte activity) will result in oxidation or reduction of the solid contact material of the ISE (located between the ion-selective membrane and the electrode support), coupled with reduction or oxidation of the electrochromic material at/ or in solution close to the other electrode. Thus, a linear dependence of absorbance/emission vs. logarithm of ionic analyte activity would be a clear advantage of this new optical system. This is a significant advantage compared to typical ion-selective optodes, with narrower response range,

Because significant limitation of the above described systems is their size, it is also desirable to use the concept of hybrid systems in micro- or nanosensors. In the micro-systems a conducting polymer (e.g. polypyrrole) microcapsule will contain solution with an agent of emission spectrum dependent on the oxidation state. In such arrangement the analyte contacting the outer shell of the conducting polymer will undergo redox reaction and thus will affect the state of the reagent present inside the capsule to result in increased observed emission. In the case of nanosensors conducting polymer nanoparticles can be used, e.g. polythiophene nanoparticles, where change of the oxidation state upon contact with an analyte will result in fluorescence change of the polymer.

The important advantage of the proposed system is electrochemical detection of analytes, high selectivity and sensitivity of electrochemical methods and, on the other hand, simple recording of optical signals (even visually). Additional possibility of further improvements is application of cameras of portable devices (smartphones, tablets) to read out the absorption/ fluorescence intensity changes. We would like to develop appropriate software for this purpose. This possibility would significantly increase mobility of analytical systems and applicability in everyday life. Moreover, they can be used as remote analytical systems, where data collected by a web camera are transferred to the workplace of the analytical personnel.