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Development and Application of an Electrochemical Sensor for Hydrogen Peroxide in Alkaline Media Based on Flash Graphene

Ema Gričar[1], Boštjan Genorio[1], Mitja Kolar[1]
[1] University of Ljubljana, Faculty of Chemistry and Chemical Technology, Večna pot 113, 1000 Ljubljana, Slovenia
ema.gricar@fkkt.uni-lj.si

Summary:
With the development of a novel microfluidic system for environmentally friendly electrochemical production of hydrogen peroxide, a need for a specifically designed electrochemical sensor for hydrogen peroxide in alkaline media (pH 13) arises. Flash graphene was used to modify the carbon screen-printed electrode together with manganese dioxide. The proposed sensor exhibited two linear ranges (1 to 100 µmolL^{-1}, and 100 to 1000 µmolL^{-1}), the sensitivity of 0.244 µAµM^{-1}cm^{-2} and the limit of detection was 0.238 µmolL^{-1}.

Keywords: flash graphene, electrochemical sensor, screen-printed electrode, carbon electrode, hydrogen peroxide.

Introduction

Electrochemical sensors stand at the frontier of the ever-expanding electrochemical research with their favorable properties. These include high selectivity and sensitivity, low cost, robustness, portability, generally wide linear range, and what is most important for the presented research – rapid response time, possible miniaturization and integration, and minimal (or none) sample preparation steps.

Hydrogen peroxide (H_2O_2) is a small inorganic molecule that is important in various fields. It is a transparent, slightly viscous liquid with a pungent odor. In biological systems, it is a byproduct of numerous enzymatic processes, as well as a signaling agent (in strictly regulated, low concentrations) [1]. Additional to its biological role, H_2O_2 is present in numerous energy conversion devices, such as fuel cells and Li-air batteries, both of which utilize the oxygen reduction reaction. Its use as an antimicrobial, bleaching, and oxidizing agent is successful partly due to the fact it yields only water and oxygen as byproducts and is as such considered environmentally friendly [2]. The anthraquinone oxidation process remains the predominant method for industrial-scale H_2O_2 production. However, the necessity for complex safety measures, additional purification due to the use of stabilizers, and lower cost-effectiveness due to the use of palladium-based catalyst and the anthraquinone carrier, prompt interest in developing decentralized, on-site H_2O_2 production. Utilizing a selective 2e$^-$ oxygen reduction reaction, this process can be carried out electrochemically. Some such systems with selective catalysts have been reported [3], whereas the aim of this work is to develop an electrochemical sensor for H_2O_2 that can be integrated into a microfluidic device for electrochemical H_2O_2, and therefore monitor its concentration in the system.

Many electrochemical sensors for H_2O_2 have been described, using various electrode materials and modifications. Often a combination of carbon nanomaterials and metal oxides are deposited onto an electrode surface to increase the surface area of the electrode and to catalyze the degradation of H_2O_2, respectively [4]. Recently, flash graphene (FG) has attracted a lot of attention [5] also as a potential new material for the use in electrochemical sensors. Its novelty and attractiveness lie in the production method, flash Joule heating, where the source material is rapidly heated using high electronic currents, as well as the fact that theoretically any carbon containing source can be turned into a high value material, namely FG. In the presented work, FG was used for the first time in combination with MnO_2 to modify carbon screen-printed electrodes and amperometrically detect H_2O_2 in alkaline (pH 13) media.

Results

Cyclic voltammetry was used to study the general electrochemical properties of modified electrodes utilizing a commonly used electrochemical probe [$K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$]. Peak heights and peak-to-peak separations indicated the optimal modification of the electrodes – 2 drop-casted layers of FG and MnO_2 dispersed in 50 % ethanol with 5 % Nafion. The expected increase in the surface area when FG is present on the electrode was indicated with an increased capacitive current and confirmed with the calculation of electrode surface areas using Randles-Ševčik equation. The surface areas for non-modified and modified electrodes were 0.1789 cm^2 and 0.2522 cm^2, respectively.

Since the target application of this sensor is continuous monitoring of H_2O_2 concentrations in a microfluidic device, where the electrochemical production of H_2O_2 takes place, the optimization of experimental parameters must be considered. Efficient, carbon-based, electrocatalysts have been shown to be active and selective towards $2e^-$ oxygen reduction reaction at high pH [3]. Therefore, to successfully integrate the produced sensor into such a device it must be efficient and stable at high pH values. The use of 0.1 M KNO_3 in 0.1 M KOH as a medium has shown satisfactory results. The detection of the analyte was carried out with hydrodynamic amperometry. The operating potential was optimized and was 0.15 V (vs Ag).

Proposed sensor has two linear ranges, first spans from 1 to 100 $\mu molL^{-1}$, the second from 100 to 1000 $\mu molL^{-1}$. Considering the expected concentration of electrochemically produced H_2O_2, the lower linear range will be in use for the present batch sensor setup. The sensitivity of the electrode in this range is 0.244 $\mu A\mu M^{-1}cm^{-2}$. Limit of detection was calculated as 0.238 $\mu molL^{-1}$.

The results of the work so far are highly satisfactory considering the harsh alkaline working conditions. First tests on the real samples have already been carried out and the results are in agreement with other detection techniques that were used for the monitoring of H_2O_2 concentration produced in the microreactor, namely optical H_2O_2 sensor, designed by Tjell *et al.* [6]. The results differ by less than ±5 %. Furthermore, the results so far indicate the possibility of multiple uses of a single screen-printed electrode.

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