SHORT COMMUNICATION

SELECTIVE VOLTAMMETRIC DETECTION OF MERCURY (II) BY A RADIATION SYNTHESIZED FEATHER ENTRAPPED-HYDROGEL MODIFIED ELECTRODE (FEHM-TRODE)

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ABSTRACT

We fabricated the feather-entrapped hydrogel-modified electrode (FEHM-trode), a chemically-modified electrode (CME) that consists of chicken feather powder (approx. 100 mm in diameter) entrapped in a radiationsynthesized polyvinilpyrrollidone (PVP) hydrogel. This metal sensor exploits the characteristics of keratin as a biologically functional material for electrochemistry (Sugawara et al., 1998) and the stabilizing and water-retention properties of hydrogels that have been crosslinked via irradiation. In a battery of heavy metal ions we tested, our feather hydrogel-trode selectively detected mercury ions (Hg²⁺) by differential pulse anodic stripping voltammetry (DPASV). Nickel, cadmium, cobalt and lead ions failed to exhibit binding with the modifier. Further work is being carried out in utilizing the hydration potential of radiation-crosslinked polymers to improve detection power of CMEs configured for detecting heavy metal contamination in water samples.

INTRODUCTION

CMEs have been recently introduced for wide application in electrochemistry, particularly the analysis of trace metals (Arrigan, 1994; Gardea-Torresdey et al., 1988). CME utilizes chemical and biological modifying moieties such as ligands, redox mediators, algae, enzymes and tissues that can accumulate metal ions as well as electroactive organic compounds. Furthermore, these sensors are deemed advantageous because of their fast analytical response, ease of fabrication, low cost and suitability for miniaturization (Wang, 2000).

Biofunctional materials can be applied as novel modifiers because of their capacity to collect specific ionic species depending on the composition of their functional groups. The possibility of using bovine horn keratin has recently been explored by the group of Sugawara (1998) and used the sensor for determining silver (I) ions in a photographic developer. Keratin is also the major structural material of chicken feathers, an abundant poultry waste product that clogs farm drainage systems and has no known use except as a poorly digestible protein source for livestock (Apple et al., 2003). Keratin contains sulfur containing amino acids like cysteine (Figure 1) which could serve as binding site for metals like mercury.
MATERIALS AND METHODS

Chicken feathers were pulverized in a laboratory mill and were sieved twice through a 100 mm-mesh. The resultant powder (50 mg) was mixed with polyvinylpyrrolidone monomer (500 mg), graphite powder (500 mg) and water (2 mL) with a mortar to obtain a paste. The paste was compacted around copper wire and smoothened with a glass spatula. The carbon paste was irradiated at 25 kGy under Co-60 to initiate polymerization. The electrode has an active surface of 0.1 cm\(^2\) (Figure 1).

Measurements were done on the Metrohm 694 VA processor connected to a three-electrode cell system: the auxiliary electrode (platinum wire), the reference electrode (Ag/AgCl electrode) and the working electrode (FEHM-trode).

Differential pulse anodic stripping voltammetry (DPASV) was executed by comparing voltammetric readings before and after pre-concentration in different analytes (cobalt, cadmium, lead, mercury and nickel at 100 mg/L). These analyte solutions were prepared by diluting each metal standard solution (1000 mg/L) obtained from J.T. Baker with deionized distilled water.

Pre-concentration was done on an open circuit wherein the sensor is dipped in an analyte solution in a cell with constant stirring for five minutes.

The parameters used for the DPASV on the different heavy metals as follows:

- U. amplitude: 50 mV
- Rot Speed: 0/min
- t. step: 0.20 s
- t. meas: 16.7 ms
- U. meas: -1000 mV
- t. pulse: 33.3 ms
- U. start: -1000 mV
- U. step: 10 mV
- U. end: 1000 mV
- Sweep rate: 50 mV/s
RESULTS AND DISCUSSION

Accumulation voltammetry of mercury (II) was achieved with FEHM-trode (Figure 2). The consistent behavior of FEHM-trode with DPASV is shown in Figure 3. A distinct peak at around 0.0 mV upon accumulation with 5 different samples containing mercury ions (Hg²⁺) using 0.01 M NaOH was observed while the four other metal ions failed to show any current response. On the other hand, all heavy metal ions used in the experiment failed to show any peak signal when 0.01 M HCl was used as supporting electrolyte.

Mercury (II) ions accumulated in the electrode matrix owing to the interaction between the sulfur atoms within the polymer network of the hydrogel and feather composite. Because the charge of mercury (II) was neutralized by ionic pairing, metal accumulation was enhanced. This mechanism could not take place with the other metal ions as shown by the absence of peaks.

In our previous experiments, repetitive use of a feather-graphite paste electrode was difficult (Tocino et al., 2003) in the absence of hydrogel entrapment. The application of radiation polymerization of PVP monomer allowed for the improvement of the mechanical and chemical properties of our bulk sensor material. In addition, it is observed that analysis time was shortened because of the rapid absorption of the analyte within the polymer. Regeneration was also very simple which involves dipping the electrode in a solution of 0.01 M EDTA.

The process of metal accumulation by the feather material is not yet fully understood. It is possible that the logic of “hard” and “soft” acid-base concept is operational in its ion complexation. The sulfhydryl group in feathers may be classified as “soft base” and forms a stable complex with mercury ion, a “soft acid”. It is also possible that ion-exchange of metal ions with the hydroxyl amino groups present in the proteins could take place.

Despite the wide promise of keratin and chicken feathers as materials for electroanalytical chemistry, there is a paucity of basic studies done in the area. Radiation-synthesized hydrogels, on the other hand, has been a richly explored subject in polymer and radiation chemistry.

REFERENCES


