Notes

Nickel-Coated Hollow-Fiber Electrode for the Electrochemical Detection of Carbohydrates

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The sensitive determination of carbohydrates by high-performance liquid chromatography (HPLC) is of practical importance. The sensitivity of the detector often limits the detection limit of the method. Since carbohydrates exhibit no strong absorption in the UV-visible range, postcolumn or precolumn derivatization is commonly used for spectrophotometric detectors.[1-5] A refractive-index detector is not sufficiently sensitive to detect carbohydrates in quantities of less than 1 nmol. An alternative approach for the sensitive detection of carbohydrates is to use electrochemical detectors. Since carbon electrodes exhibit no response to carbohydrates, metallic and metal-oxide-modified electrodes have been utilized instead by a number of research groups.[6-21] The detection of carbohydrates at pmol levels has been achieved with electrochemical detection systems.

A thin-layer-type flow cell is generally employed for electrochemical detectors. Since the stream flowing over a flat electrode surface in the cell has a 10 – 100 μm thickness, only a small fraction of the analytes participates in the electrical response. To enhance the electrolytic efficiency, working electrodes made of bundled carbon fibers have been developed.[22,23] An electrolytic efficiency of 100% was achieved for the oxidation of catecholamines with the electrode because of the extremely small dead volume of the cell and the large surface area of the electrode.[22]

Recently, a metal-coated hollow-fiber (MCH) has been developed by electroless plating.[24] The MCH prepared by coating a metal such as Ni, Cu, Pt or Au on the surface of a polypropylene hollow-fiber has an extremely large surface area due to its porous structure. The application of MCHs to an electrochemical detector for HPLC was expected to allow a high electrolytic efficiency in the electrocatalytic oxidation of carbohydrates by passing an effluent through the micropores.

In the present study, a nickel-coated hollow-fiber (Ni-MCH) was evaluated as a working electrode by means of cyclic voltammetry, and applied to the electrochemical detection of carbohydrates with HPLC.

Experimental

Reagents and apparatus

All of the chemicals used were of reagent grade and commercially available. Glucose was dissolved in 0.15 M NaOH for cyclic voltammetry and in water for HPLC. A 0.15 M NaOH solution as a mobile phase was used after filtration through a cellulose acetate membrane filter (0.45-μm pore size; Advantec Toyo Co., Tokyo). The NaOH solution was protected from carbon dioxide uptake by a soda lime trap on the mobile-phase reservoir.

Cyclic voltammetry was conducted with an HECS 311B potentiostat and an HECS 321B potential sweep unit (Fuso Co., Tokyo). HPLC was performed with a Hitachi L-6010 pump with a Rheodyne 9125 injector (20 μl) and a Dionex AS-7 anion-exchange column. The electrochemical detector was fabricated in a three-electrode configuration: an Ni-MCH working electrode (inner diameter, 1.0 mm; outer diameter, 1.6 mm; length, 5 mm), an Ag/AgCl reference electrode (Model 4201; Denki Kagaku Keiki Co., Tokyo) and a Pt coil counter electrode. The potential of the working electrode was held at +0.45 V *vs.* Ag/AgCl for the *in-situ* formation of nickel oxide. A more positive potential is preferable for the oxidation of carbohydrates. Both the background current and the noise fluctuation, however, increased along with the potential. The effluent was introduced into Ni-MCH, and allowed to flow out through the pores in the wall of the electrode. The output signal was recorded with a Hitachi D-2500 chromato integrator.

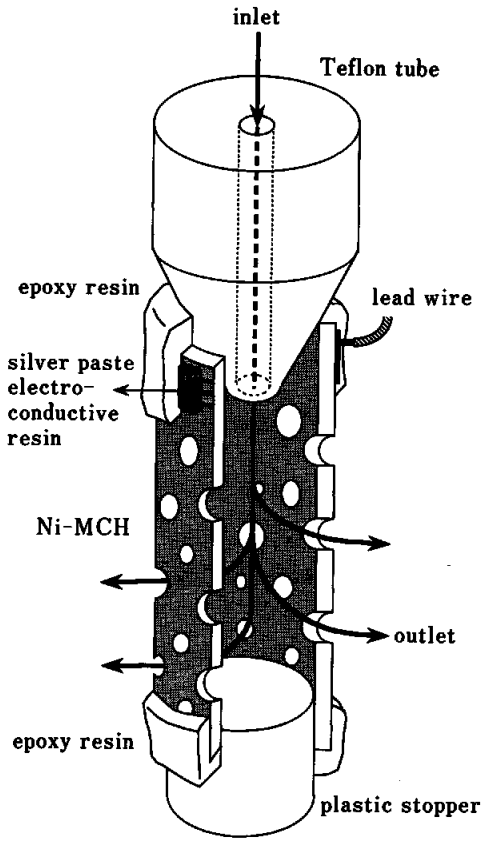

Fig. 1 Schematic representation of the nickel-coated hollow-fiber electrode for HPLC.

Ni-MCH electrode

The Ni-MCH (pore size: *ca.* 6 μm (outside), *ca.* 0.6 μm (inside)) was donated from Nikko Industry Co. (Kanagawa). Both the inside and outside of a poly-propyrene hollow-fiber were coated with a 12.5-μm thick Ni layer. After the Ni-MCH was cut to an appropriate length, one end was connected to a lead wire using a silver-paste electroconductive resin (Dotite type D-550; Fujikura Chemicals Co., Tochigi). The Ni-MCH electrode used for cyclic voltammetry was prepared by fixing the side connected to a lead wire on a tip of a glass tube with epoxy resin (Epoxylite R-86; The Epoxylite Co., CA, USA).

In order to introduce an effluent from an anion-exchange column into the inside of the Ni-MCH electrode for HPLC, a Teflon tube (inner diameter, 0.5 mm; outer diameter, 1.5 mm) with a sharpened tip was inserted into the inlet of the Ni-MCH and fixed with epoxy resin. The opposite end of the Ni-MCH was sealed with a plastic stopper, so that a stream of effluent was forced to flow from inside to outside through the porous wall of the electrode (Fig. 1).

Results and Discussion

Fleischmann *et al.*[25,26] have reported that glucose is oxidized catalytically by an active Ni(III) oxide (NiOOH) at a Ni rod electrode, where two electrons participate in the electrocatalytic oxidation of one hydroxyl group of glucose and Ni(III) oxide is reduced to Ni(II), *e.g.*, $Ni(OH)_2$. Considering the mechanism at a Ni rod electrode, it appeared that the oxidation of glucose at Ni-MCH is electrocatalytic. The electric resistance of the Ni-MCH used was found to be 2–5 Ω/cm. The cyclic voltammograms obtained with a 5-mm long Ni-MCH electrode in 0.15 M NaOH solutions with and without added glucose are shown in Fig. 2. The voltammogram obtained in a blank solution exhibited a broad cathodic peak due to the reduction of Ni(III) formed during the anodic scan. The height of the reduction peak at *ca.* +0.1 V decreased almost linearly with the concentration of glucose in the solution.

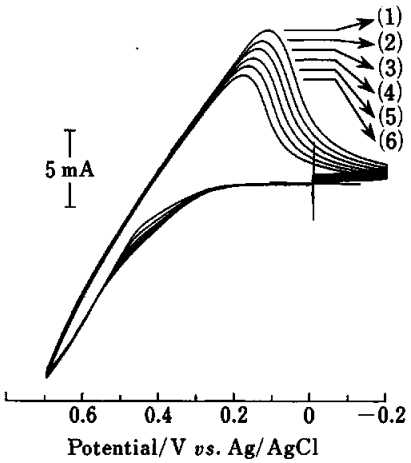

Fig. 2 Voltammetric responses of the nickel-coated hollow-fiber electrode at a scan rate of 100 mV/s in the absence (1) and presence of 1 (2), 2 (3), 3 (4), 4 (5) and 5 (6) mM of glucose in 0.15 M NaOH.

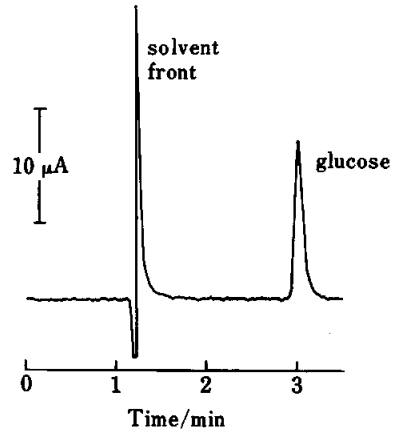

Fig. 3 Chromatograms of 1 nmol glucose in water with the Ni-MCH detector: potential, +0.45 V *vs.* Ag/AgCl; column, Dionex AS-7 anion exchange column; mobile phase, 0.15 M NaOH; flow rate, 1.0 ml/min.

In order to use a microporous Ni-MCH electrode for the detection of glucose, it is necessary to pass the sample solution through the pores in the wall of the Ni-MCH. The permeability of water through the porous wall of Ni-MCH was tested by means of suction at 8.0×10^4 Pa. Water did not permeate through the hydrophobic wall of a bare polypropylene hollow-fiber. On the other hand, the Ni-MCH allowed water to permeate through the hydrophilic porous wall under controlled pressure.

The Ni-MCH electrode connected to the pump for HPLC (without a column) ensured the flow of the mobile phase at a flow rate of 1.0 ml/min under a pressure of *ca.* 4.9×10^5 Pa through the porous wall of the electrode.

A chromatogram of 1 nmol glucose with the present detector is shown in Fig. 3. The height and area of the oxidation peak obtained with the present detector were 13.8 μA and 94.0 μC, respectively. In addition to glucose, galactose, fructose and saccharose were also detected with this system. The peak current for 1 nmol of glucose with the present detector (surface area, *ca.* 2000 mm^2; cell volume, 0.31 μl) was much larger than those reported by Reim and Van Effen[6] with a Ni tubular electrode (surface area, 23.78 mm^2; cell volume, 9.45 μl) and with a thin layer flow cell detector (dual Ni electrodes; surface area, 14.14 mm^2; cell volume, 1.53 μl). The amount of electrocatalytically oxidized hydroxyl groups was calculated from the observed peak area, assuming that two electrons are exchanged in the catalytic oxidation process.[25,26] It was found that 487 pmol of the hydroxyl group in 1 nmol of glucose injected was oxidized. This high electrolytic efficiency is due to the microporous structure of the present electrode. The relative standard deviation for three determinations of 1 nmol glucose was found to be 0.11%. The detection limit for glucose, defined as a signal-to-noise ratio (S/N) of 3, was 25 pmol. This value is inferior by about 5 times compared to that reported by Reim and Van Effen[6] with a Ni tubular detector.

The reasons for the unsatisfactory detection limit with the present detector are a high noise fluctuation (115 nA) and broad peak shapes compared with those for dual Ni-rod and Ni-tublar electrodes. In order to improve the detection limit of the present system, the use of a narrower hollow-fiber to reduce the inner volume of the MCH electrode and the modification of the electroless plating process to reduce the electric resistance of the material are currently under way.

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