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Electrochemistry Communications 7 (2005) 1205–1208

electrochemistry communications

www.elsevier.com/locate/elecom

Integration of electrochemical generator and detector of nitric oxide with the aid of the iron porphyrin

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Received 27 July 2005; accepted 16 August 2005
Available online 27 September 2005

Abstract

An electrochemical cell of generating nitric oxide (NO) was constructed in order to realize the catalytic reaction of nitrite by iron porphyrin [Y. Chi, J. Chen, K. Aoki, Inorg. Chem. 43 (2004) 8437]. The cell was composed of the generator of the iron porphyrin-including Nafion®-coated electrode, the ion-exchange membrane, and the electrochemical detector of NO. The reduction of iron porphyrin in the presence of nitrite at the generator coordinates nitrite to form the NO-included complex, of which oxidation releases NO. The water-dissolved NO diffused to the detector through the membrane to block nitrite. It was detected by voltammetry with the aid of the oxidative catalytic reaction of iron porphyrin.

Keywords: Electrochemical generator cell; Amperometric detection; Nitric oxide; Nitrite; Iron porphyrin; Catalytic reaction

1. Introduction

Nitric oxide (NO) plays a key role in physiological processes [1,2], such as vasodilatation, inhibition of platelet aggregation, neurotransmission and cytotoxicity. A controlled release of NO at a given location is of interest in clinical trials. Polymeric films capable of releasing NO have been developed by means of immobilization of NO adducts [3] and reduction of nitrite [4].

We suggested previously that NO could be generated electrochemically from nitrite with the help of iron porphyrin [5,6]. The generation is based upon the mechanism in which the electrochemical reduction of iron porphyrin in nitrite solution forms irreversibly NO-included iron complexes that release NO by oxidation [6]. This process allows us to construct an electrochemically releasing apparatus for NO if iron porphyrin can be immobilized in an electrode-modified film as a catalyst in nitrite solution. Since the generation includes two potential steps of the formation of the NO-complexes and the release of NO, it is a batch process. In order to assess the performance of generating NO, it is necessary to detect time-variations of generated NO, like amperometric detection. NO has been detected electrochemically not only by direct redox reaction [7] but also by use of some catalysts, such as nickel porphyrin [8], iron porphyrin [6] and Dawson-derived complexes of polyoxometalate [9]. The catalytic oxidation current of NO in the presence of iron porphyrin has been enhanced 10 times more than the diffusion-controlled current [5].The amperometric detection of NO has often supported by Nafion® [10] and cellulose acetate [11] films in order to avoid electrode fouling. Basic electrode behavior of NO has been documented in the light of interaction of electrodes [12].

Now we are at the stage of both generating NO electrochemically and of detecting NO electrochemically. However, nitrite as a reactant of NO hinders the detection of NO [13–15]. The problem may be circumvented by isolating NO from nitrite by using anion-exchange membrane at the cell, in which the generator and the detector are sandwiched. This communication reports the fabrication of an electrochemical generation-detection unit.

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doi:10.1016/j.elecom.2005.08.026

2. Experimental

5,10,15,20-Tetrakis(*N*-methylpyridinium-4-yl)-21H,23H-porphyrin,tetrakis (*p*-toluene sulfonate), abbreviated as H_2(TMPyP) 4Ts, was used for preparation [16] of Fe^{III}(TMPyP)]Cl_5. Nafion® 117 solution of 5 wt% (Wako), tetrabutylammonium bromide (Wako), sodium nitrite (Wako) and other chemicals were of analytical grade. 1.0×10^{-3} mol dm^{-3} [Fe^{III}(TMPyP)]Cl_5 solution was prepared as described previously [5]. The aqueous medium was 0.1 M (= mol dm^{-3}) sodium phosphate buffer solution (PBS) at pH 7.4, prepared with twice-distilled water.

NO solutions were prepared by bubbling different given concentration of NO gas (Nippon Sanso, Japan) into deoxygenated solutions for 30 min. The concentration was evaluated from Ostwald's solubility coefficient for a given partial pressure of NO [17].

The whole generation-detection apparatus was composed of the generator cell, the detector cell and the separator, as is illustrated in Fig. 1. Each cell, made of polymethacrylate, had an inlet and an outlet of solution, the Ag|AgCl reference electrode, and a hole of mounting the working electrode. The two cells were put together with bolts, sandwiching the ion-exchange membrane 0.5 mm in thickness and two holed separators each 0.13 mm in thickness. The membrane was formed by coating Nafion® solution five times on the polytetrafluoroethylene membrane (0.2 μm pore size, 80% porosity, Millipore) and by reinforcing the dried membrane with the molecular porous membrane (MWCO 12000, Spectra/Por). This assembled membrane plays a role in blocking the transfer of nitrite and in passing dissolved NO to the detector cell. The separator was parafilm (NKO). The inlet and the outlet pipes were made of stainless steel. They were used also for a counter electrode.

A mixture of 0.25 wt% Nafion® 117 diluted with methanol and 2.0 wt% tetrabutylammonium bromide was dropped on the polished glassy carbon (GC) electrode, and was dried at room temperature. The thickness of the dried film was ca. 10 μm. The Nafion-coated electrode was immersed in 1 mM Fe^{III}(TMPyP)]Cl_5 PBS solution for 30 min and was rinsed with water. The porphyrin-modified electrode was mounted in the generator block with a help of shielding tape.

Potentio/Galvanostat (Model 1112, Huso, Kawasaki) under a control of a computer was used for all electrochemical experiments. Conventional voltammetry was made at GC disk electrode 3 mm in diameter in the one compartment cell. The Pt wire and the Ag|AgCl electrode were used as a counter electrode and as a reference electrode, respectively. Voltammetric measurements were carried out by using a three electrode system.

A 10^{-5} M nitrite solution was pumped into the left cell (generator). Potential −0.4 V was applied to the generator for 5 min and then switched to 0.4 V. NO will be released from W_1 to the solution. It will pass through the ion-exchange membrane selectively. In order to detect NO at the detector, linear sweep voltammetry was set out 30 s after the potential application of 0.4 V to the generator.

3. Results and discussion

Cyclic voltammograms of the Fe^{III}(TMPyP)-included PBS solution showed the diffusion-controlled anodic and the cathodic peaks at −0.18 and −0.11 V, respectively at the naked glassy carbon electrode (Fig. 2(c)). The Fe^{III}(TMPyP)]-modified electrode exhibited the redox peaks at −0.07 and −0.14 V, as is shown in Fig. 2. Both the peak currents were proportional to the potential scan rates less than 0.25 V s^{-1}, indicating the surface wave. The redox charge estimated from the area of the peak was 11 μC cm^{-2}, which corresponds to 0.012 mM in the Nafion® film (10 μm thickness). When $NaNO_2$ was added to the solution, both redox waves shifted by −40 mV and a new anodic wave appeared at 0.38 V. The new wave has been demonstrated spectroelectrochemically to be ascribed to the formation of $[Fe^{II}(NO)(TMPyP)]^{4+}$ [18]. The corresponding cathodic wave is overlapped with the wave at −0.14 V.

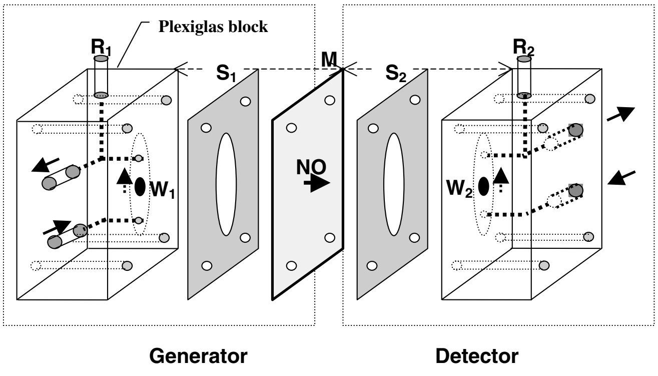

Fig. 1. Illustration of the cell structure, where W_1 and W_2 are the working GC electrodes, M is the assembled membrane, and S_1 and S_2 are separators.

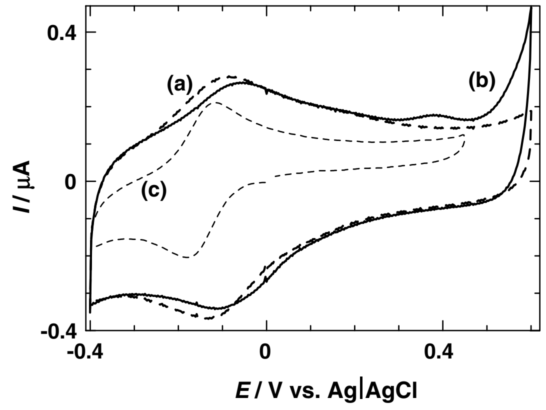

Fig. 2. Voltammograms at the Fe^{III}(TMPyP)-modified electrode in the PBS solution (a) without (dotted curve) and (b) with (solid curve) 10^{-5} M $NaNO_2$ at the potential scan rate of 0.1 V s^{-1}. (c) cyclic voltammogram of the Fe^{III}(TMPyP)-included BPS solution at GC electrode.