A Flow-Through Detector Based on the Photoelectrochemical Reaction of an Anthraquinone-2,6-disulfonate Dianion/ Cationic Perfluoro Polymer Complex

Naoyoshi EGASHIRA,* Toshirou FUJISAWA, and Kazuya OHGA*
Department of Environmental Chemistry and Engineering, Faculty of Engineering, Oita University, 700 Dannoharu, Oita 870-11
(Received December 22, 1988)

Synopsis. A glassy carbon electrode modified with an anthraquinone-2,6-disulfonate dianion/cationic perfluoro polymer complex was used as the working electrode of a flow-through detector based on a photoelectrochemical reaction. Several α-amino acids gave anodic photocurrents. The photocurrent-peak area of proline increased linearly with the concentration in the range of 0.5—10 mmol dm^{-3} and the detection limit (S/N=2) was 5×10^{-5} mol dm^{-3}.

In a previous paper,[1] we reported a new electrochemical flow-through detector which was equipped with a working electrode modified with polystyrene having pendant anthraquinone groups. The principle of detection proposed involves photochemical reduction of the anthraquinone moiety by analytes and electrochemical oxidation of the resulting reduced form of the anthraquinone on the electrode to give an anodic current. The detector has the advantage of permitting direct analyses of α-amino acids and amines which are undetectable by conventional electrochemical detectors without pretreatment.[2,3] However, a dimethyl sulfoxide solution that is rarely used for HPLC analysis of amino acids was required as the mobile phase because of the hydrophobicity of the polymer used. In the present paper, we described a modified electrode favorable for an aqueous mobile phase using a hydrophilic polymer, a complex (Fig. 1) formed from a cationic perfluoro polymer (CPF) and disodium anthraquinone-2,6-disulfonate (ADS).

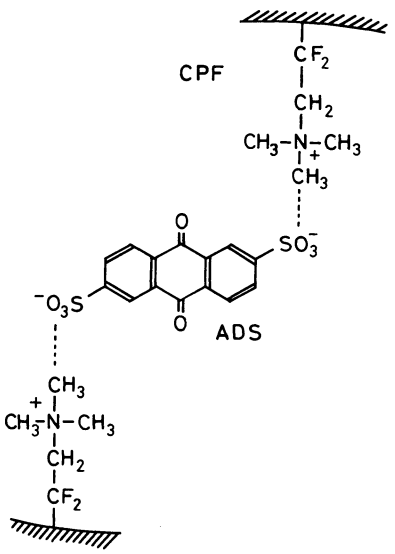

Fig. 1. CPF/ADS complex.

Experimental

A CPF film (Toyo Soda Co.) was finely cut and mixed with H_2O/CH_3OH/2-propanol (volume ratio, 1:1:1).[4] The mixture was refluxed with stirring at 70 °C for 36 h and filtered. The concentration of CPF in the filtrate was estimated to be 0.84 mg cm^{-3} on evaporating the solvent and weighing the remaining CPF. A given amount of ADS was added to 1 cm^3 of the CPF solution to yield a complex solution.

A glassy carbon disk (Tokai Carbon GC-30S) of 0.6 cm in diameter was coated with 0.1 cm^3 of the complex solution and dried under reduced pressure. The polymer-film thickness of the modified electrode obtained was evaluated to be about 3 μm with an Ono Sokki DG-215 digital dial gauge having a spindle. The flow-through cell used was the same as reported previously[1] and was equipped with a glass window (Corning) to cut off light of wavelengths shorter than 310 nm. The light source was a 500-W xenon lamp (Shimadzu). The light intensity was estimated to be 3.2 μW cm^{-2} with a Tokyo Kougaku Kikai UVR-365 exposure meter which responds to light from 310 to 400 nm. The modified electrode, a platinum plate (0.15 cm^2), and a Ag/AgCl electrode were employed as the working, counter, and reference electrodes, respectively. A potential of 0.2 V was imposed on the working electrode in order to reoxidize the reduced form of ADS. A N_2-bubbled phosphate buffer solution (0.1 mol dm^{-3}, pH 11) was allowed to flow through the cell at a rate of 1.0 cm^3 min^{-1}

Results and Discussion

The cyclic voltammogram of the modified electrode showed reversible redox peaks around −0.6 V as shown in Fig. 2, indicating that the electrode can be used effectively to detect the reduced form of ADS. A potential difference between the redox peaks of about 0.2 V was larger than those for electroactive species immobilized on electrodes in the form of monolayers,[5] probably because of an uncompensated ohmic resistance of the polymer film.[6] A maximum anodic peak current was obtained with a film prepared from 1.2 mg of ADS and 1 cm^3 of the CPF solution; further addition of ADS to the CPF solution did not significantly increase the photocurrent, as is described below.

Figure 3 shows the anodic photocurrents resulting from the intermittent injection (20 mm^3) of a buffer solution of proline (1 mmol dm^{-3}) into the cell. The peak area of the current was found to be reproducible at about ±3% and to increase linearly with the concentration of proline in the range of 0.5—10 mmol dm^{-3} (Fig. 4). The detection limit was 5×10^{-5} mol dm^{-3} (S/N=2) comparable to that of a differential refractive index detector.[7]

Other α-amino acids also gave photocurrent peaks,

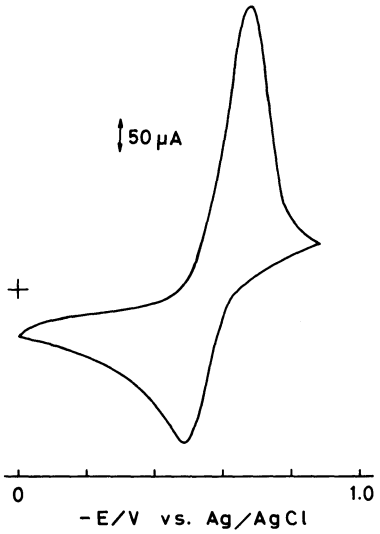

Fig. 2. Cyclic voltammogram of a modified electrode (area: 0.283 cm^2) with a CPF/ADS complex in 0.1 mol dm^{-3} phosphate buffer (pH 11). The sweep rate was 0.1 V s^{-1} and the weight ratio of ADS to CPF was 1.4.

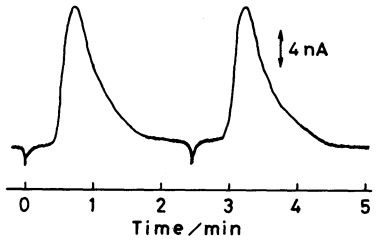

Fig. 3. Photocurrent response of the modified electrode (ADS/CPF weight ratio=1.4) induced by intermittent injection of proline (10 mmol dm^{-3}, 20 mm^3).

though the currents were lower than that of proline: The peak areas of methionine, lysine, histidine, and valine were 0.14, 0.14, 0.10, and 0.04 μC, respectively, when the same molar quantities as that of proline (0.2 μmol, 0.33 μC) were injected. In addition, it is important to note here that dark currents were not observed for these amino acids. These results suggest

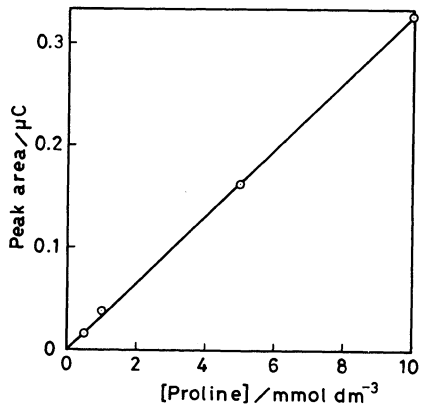

Fig. 4. A calibration curve of the peak area vs. the concentration of proline. Injection volume was 20 mm^3.

that the CPF/ADS-modified electrode is applicable to HPLC analysis of such electroinactive amino acids with aqueous mobile phases.

The proline peak area was unchanged for about 7 h after an initial unstable period (2 h), but subsequently, decreased gradually, probably owing to loss of ADS from the complex. Thus, the development of a more stable photoresponsive polymer would be required for this type of detector to have long life.

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 62750768 from the Ministry of Education, Science and Culture.

References

1) N. Egashira, T. Fujisawa, and K. Ohga, *Denki Kagaku*, **57**, 65 (1989).
2) K. Shimada, M. Tanaka, and T. Nambara, *J. Chromatogr.*, **227**, 445 (1982).
3) W. A. Jacobs and P. T. Kissinger, *J. Liq. Chromatogr.*, **5**, 881 (1982).
4) N. Oyama, T. Ohsaka, and T. Okajima, *Anal. Chem.*, **58**, 979 (1986).
5) A. J. Bard and L. R. Faulkner, "Electrochemical Methods," John Wiley & Sons, New York (1980), p. 204.
6) P. Daum and R. W. Murray, *J. Phys. Chem.*, **85**, 389 (1981).
7) M. M. Munk, *J. Chromatogr. Sci.*, **8**, 491 (1970).