



A flow electrolysis cell with a thin aqueous phase and a thin organic phase for the absolute determination of trace ionic species



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ABSTRACT

A novel thin-layer electrolysis flow cell based on the ion transfer at the liquid|liquid interface was proposed for the absolute determination of a sub-nanomole ionic species. By using the conducting polymer-coated electrode as an electrode in organic phase, the flow cell was developed as a laminate structure with a thin aqueous layer and a thin organic layer, which were set between an Ag/AgCl electrode and the conducting polymer-coated electrode. Its simple structure made it possible to miniaturize the flow cell, and the required sample volume was reduced to only 1 μl . In the present electrolysis cell, both quantitative extraction and quantitative back-extraction of total amount of the ionic species were achieved. This advantage was applied to two methods for absolute determination. One is that by flow injection method, and the other is that by pre-concentration into the thin organic phase followed by back-extraction of the species from the thin Org to the thin aqueous phase (i.e., the stripping technique). In these methods, coulometrical determination of sub-nanomol ionic species was realized without a calibration curve.

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1. Introduction

The electrochemical method is the most powerful method to determine amounts of trace species; in this method, the molar amount is directly estimated according to Faraday's law, and the weight measurement of the reference analyte material, which is necessary for preparing calibration curve, is not required (i.e., this method provides an absolute determination). In the last decade, the absolute determination of redox-inactive species based on the voltammetry of the ion transfer at the liquid|liquid interface was proposed [1–3]. In this method, the distribution ratio of an ionic species between the aqueous phase, W, and the organic phase, Org, is controlled by applying an interfacial potential, and the amounts of ionic species transferred from W to Org are simultaneously detected as current signals. Based on the current for the ion transfer at the W|Org interface, a redox-inactive ion can be coulometrically determined. To date, two types of electrolysis flow cell have been reported for absolute determination based on the ion transfer at the W|Org interface. One is a spacer-type flow cell with a polyester film in which a flow path for W was formed [1], and the other is a tube-type flow cell which has flow path for W between a porous polytetrafluoroethylene tube and an Ag/AgCl wire [2]. In both cells, W was designed to be thin, to attain

quantitative transfer of an analyte ion from W to Org. The absolute determination of a redox-inactive ion using the injection method [1,2], the precise absolute determination using the continuous flow method [2,3] and the selective absolute determination by the addition of an ionophore into Org [3] were realized in these cells.

For the absolute determination of trace species, it is necessary either to decrease the sample volume to the microliter level or to reduce the detectable concentration to the micromolar level. Moreover, for the analysis of precious samples, it is highly desirable to be recovered as an aqueous sample solution after the absolute determination, so that it can be subjected to further analysis. However, in the previous electrolysis cells, the detectable concentration range was rather high (e.g. 0.5–2 mM; $M = \text{mol dm}^{-3}$) and the required sample volume was rather large (e.g. 20–200 μl) [1,2]. The sample ion, which is transferred to the Org of the cell by the coulometric measurements, cannot be back-extracted from Org to W, because of the large volume of Org. Therefore, the previous electrolysis cells are not suitable for absolute determination of trace amounts of precious species.

A major barrier to the decrease of the sample volume or the fabrication of the cell with a thin Org layer is the complicated structure of the electrode for Org employed in the previous electrolysis cells, which is a liquid membrane-type electrode with an inner aqueous solution. In regard to this problem, a conducting polymer-coated electrode is one of the electrode types that are suitable for thin-layer electrolysis cells. The conducting

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polymer-coated electrode is a simple solid electrode, the structure of which contributes to formation of a stable thin Org layer. The conducting polymer-coated electrode have been applied to all-solid ion-selective electrodes with a thin organic membrane [4–9], and as working electrodes for the stripping analysis of ionic species based on the ion transfer at the W|Org interface [10–14]. Recently, it was found that conducting polymer-coated electrodes could be applied as the electrode having functions of both the reference electrode and the counter electrode in Org [15]. In the present work, by using the conducting polymer-coated electrode as an electrode in Org, the electrolysis flow cell was developed as the miniaturized flow cell with both a thin W layer and a thin Org layer for the absolute determination of trace ionic species. In the present cell, the required sample volume could be reduced to only 1 μl , and quantitative extraction and quantitative back-extraction were achieved. By employing the present cell, two types of absolute determination were carried out. One is that by the flow injection method, and the other is that by pre-concentration into the thin Org and back-extraction of the species from the thin Org to the thin W (i.e., the stripping technique), which is achieved by changing the applied potential. In these methods, determination of a sub-nanomol ionic species was realized without a calibration curve.

2. Experimental section

2.1. Chemicals

1,2-Dichloroethane (DCE) was purified by shaking with distilled water three times to remove HCl impurities [16], followed by drying with activated molecular sieves (3A 1/16, Wako Pure Chemical Industries, Ltd., Osaka, Japan). 2-Nitrophenyl octyl ether (NPOE) (Lot CS007, Dojindo Molecular Technologies, Inc., Kumamoto, Japan) was purified by shaking with a 0.1 M NaOH aqueous solution (repeated three times) to remove a yellow impurity, and washing with distilled water (repeated three times), following a method described in previous literature [17]. Poly(3,4-ethylenedioxythiophene) (PEDOT) was prepared by the electropolymerization of 3,4-ethylenedioxythiophene (EDOT) (Sigma–Aldrich, St. Louis, US) in DCE. Bis(triphenylphosphoranylidene)ammonium perchlorate (BTPPAClO₄) was obtained as a white precipitate by mixing a methanol solution of BTPPACl with a methanol solution of NaClO₄. The BTPPAClO₄ was washed with methanol and with distilled water, and recrystallized twice by adding distilled water to the acetonitrile solution of BTPPAClO₄. Tetrakis [3,5-bis(trifluoromethyl)phenyl]borate salt of BTPPA⁺ (BTPPATFPB), which was the supporting electrolyte in the organic phase of the electrolysis cell, was prepared from BTPPACl and NaTFPB according to the procedure described previously [18]. NaTFPB was synthesized based on the Grignard reaction [19,20], and purified with the procedure described in the literature [18]. The TFPB salt of tetrapentylammonium (TPenATFPB), which was used for a reference electrode in the preparation of the conducting polymer-coated electrode, was also prepared from tetrapentylammonium chloride, TPenACl, and NaTFPB according to the same procedure as that used to prepare BTPPATFPB. The electrolysis flow cell was held in poly(dimethylsiloxane) (PDMS) (Sylgard® 184, Dow Corning Toray Co., Ltd., Tokyo, Japan). The chloride salt of tetraethylammonium (TEACl) (Lot No. KLP0696, Wako Pure Chemical Industries, Ltd., Osaka, Japan) was used as a model ion. Sodium tetraphenylborate (99.5%, Dojindo Molecular Technologies, Inc., Kumamoto, Japan) was employed for the standardization of TEACl. The other reagents used were of analytical grade.

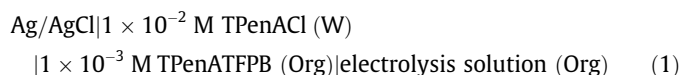
2.2. Standardization of TEACl

TEA⁺ was used as a model ion in coulometric electrolysis because TEA⁺ is semi-hydrophobic and a well-known ion in

voltammetry at the liquid|liquid interface. The solid TEACl is deliquescent and contains some water in itself. Therefore, the TEACl solution should be precisely determined. The actual quantity of TEACl in the reserved solution was estimated by conductometric titration, which was carried out with a conductivity meter (CM-60S, TOA Co., Kobe, Japan). 20 ml of a sample solution containing 10^{−3} M TEACl was titrated with an aqueous solution of 10^{−3} M sodium tetraphenylborate, and the conductivity was monitored using a conductivity cell (cell constant: 0.975 cm^{−1}). The equivalence point was defined from the inflection point in the slope. The correction factor (*f*), which was defined as the ratio of actual quantity to apparent quantity, of TEA⁺ in the sample solution was estimated to be 0.93 ± 0.01 (95% confidence interval, *n* = 3). In analysis of coulometric determination, the actual concentration of TEA⁺ (*C*_{TEA⁺}^{*}) was calculated from the apparent concentration (*C*_{TEA⁺}) and *f* by means of *C*_{TEA⁺}^{*} = *fC*_{TEA⁺}.

2.3. Preparation of the electrodes

The PEDOT-coated Pt electrode (PEDOT-Pt) was adopted as a conducting polymer-coated electrode. A PEDOT-Pt was prepared according to the procedure described in a previous paper [15]. The electrolytic cell used for the preparation of the PEDOT-Pt was a three-electrode system with a Pt-film working electrode, a Pt-mesh counter electrode and a TPenA-selective reference electrode (TPenA-ISE). Here, TPenA-ISE had the following composition:



PEDOT was electrically deposited on both side of a Pt electrode by immersing a Pt film (20 mm × 10 mm, 50 μm thickness) in DCE containing 0.1 M EDOT and 0.1 M BTPPAClO₄, and by oxidizing EDOT without stirring the solution at an electrode potential *E* of 2.0 V vs. TPenA-ISE for 20 s. Before the electrodeposition, the electrolysis solution was deaerated by passing argon gas through DCE for 30 min. The PEDOT film was obtained as an oxidized PEDOT doped with ClO₄[−]. The electric charge required for reduction or oxidation of total amount of the PEDOT film was 5–7 mC cm^{−2}. After the electrodeposition of the PEDOT film, the deposited PEDOT film was completely reduced by the application of an *E* of −1.0 V for 60 s, and the ClO₄[−] in the PEDOT film was undoped. To dope TFPB[−] into the PEDOT and to remove the residual ClO₄[−], potential scans were carried out in DCE containing 0.1 M BTPPATFPB in the potential range from −0.8 to 1.5 V; the scans were repeated 15 times with a potential scan rate of 0.1 V s^{−1}, while the solution was stirred. In this procedure, deaeration with argon gas was not required. The oxidation ratio of the PEDOT-Pt was chronocoulometrically adjusted to be 50% in DCE with 0.1 M BTPPATFPB, by oxidizing whole of the PEDOT at 0.6 V, and then by reducing it partially at −0.4 V. Before the measurements, the obtained PEDOT-Pt was dipped in NPOE containing 10^{−3} M of BTPPATFPB for at least 1 h.

2.4. Construction of the thin-layer flow cell

In the present thin-layer flow cell, NPOE was employed as the Org phase. NPOE has low vapor pressure, high viscosity (13.8 mPa s) [21], and low solubility in water (2.01 $\mu\text{mol dm}^{-3}$) [22]. The thin layer of NPOE was stable and durable in the flow system.

The thin-layer flow cell is shown in Fig. 1. An Ag film (20 mm × 10 mm, thickness of 20 μm) coated with AgCl and the 50% oxidized PEDOT-Pt were employed as electrodes for the W and NPOE, respectively, which served as both reference and counter electrodes. The thin-layer flow cell was composed of an upper

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