



Short communication

## Liquid-junction-free system for substitutional stripping voltammetry using a closed bipolar electrode system



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## ABSTRACT

A liquid-junction-free electrochemical system has been developed for substitutional stripping voltammetry (SSV). SSV is a type of stripping analysis that changes the redox current to metal deposition. Generally, SSV requires a liquid junction to maintain electrical conductivity between separated cells. In this report, a closed bipolar electrode system (cBPES) was used to perform SSV without a liquid junction. In this system, electrical conductivity between separated cells was maintained using driving electrodes inserted into each cell. We demonstrated quantification of *p*-aminophenol (pAP) using a liquid-junction-free system for SSV. We investigated the effect of electrode area ratio on the BPE and the concentration ratio of redox species present in each cell. Then, we calibrated the pAP. A linear relationship between pAP concentration and SSV electrical charge was successfully obtained using our liquid-junction-free system, based on cBPES. This novel analytical system is a promising method for the fabrication of a compact SSV sensor for highly sensitive detections.

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## 1. Introduction

Substitutional stripping voltammetry (SSV) is a highly sensitive electrochemical analytical method with pre-electrolysis step and stripping step [1–6]. The pre-electrolysis step is conducted with a galvanic cell (Fig. 1A), in which the oxidation of the analyte molecular at the anode (reaction electrode; BPr) in a cell (reaction cell) occurs concurrently with the reduction of metal ions at the cathode (deposition electrode; BPd) in the other cell containing metal ions (deposition cell). The amount of the deposited metal is obtained with anodic stripping voltammetry (ASV) in the stripping step. Because the concentration of the analyte molecules is related to the amount of the deposited metal, we can obtain the concentration of the analyte molecule with SSV. Taking advantages of the high sensitivity of the SSV, applications of SSV to the detection of small amount

of analyte are demonstrated including an endotoxin sensor [3], a sensor to estimate the oxygen consumption rate of a small fish [4] and an immune assay chip for carcinoembryonic antigen [5]. To perform the pre-electrolysis step of the SSV, a liquid junction is required to provide ion conductivity between two electrochemical cells. However, the use of a liquid junction often causes problems such as clogging and undesirable ion leakage. In particular, for compact-type measurement systems, it is difficult to fabricate a robust liquid junction [6].

To overcome this problem, we propose a liquid-junction-free system for SSV using a couple of electrodes (driving electrodes 1 and 2 in Fig. 1A) connected to the potentiostat instead of a liquid junction to provide the electrical conductivity for the two cells. Fig. 1A shows a basic design of the liquid-junction-free system for SSV. Similar to conventional SSV, reaction cell and deposition cell are connected by BPr and BPd. The electrons generated by the oxidation of the analyte on the BPr are transferred to the BPd, resulting in metal deposition on the BPd. Instead of a liquid junction, we inserted driving electrodes in each cell and connected the electrodes to a potentiostat to act as the counter electrode (CE) and working electrode (WE). A reference electrode (RE) was inserted in a same cell as the CE. By applying an appropriate voltage between the RE in a cell and a driving electrode in another cell, the electrochemical reactions at two driving electrodes compensate for the reactions at the BPr and BPd, and supply the ions to maintain electrical neutrality of the cells. The cell configuration shown in Fig. 1A is the same as a

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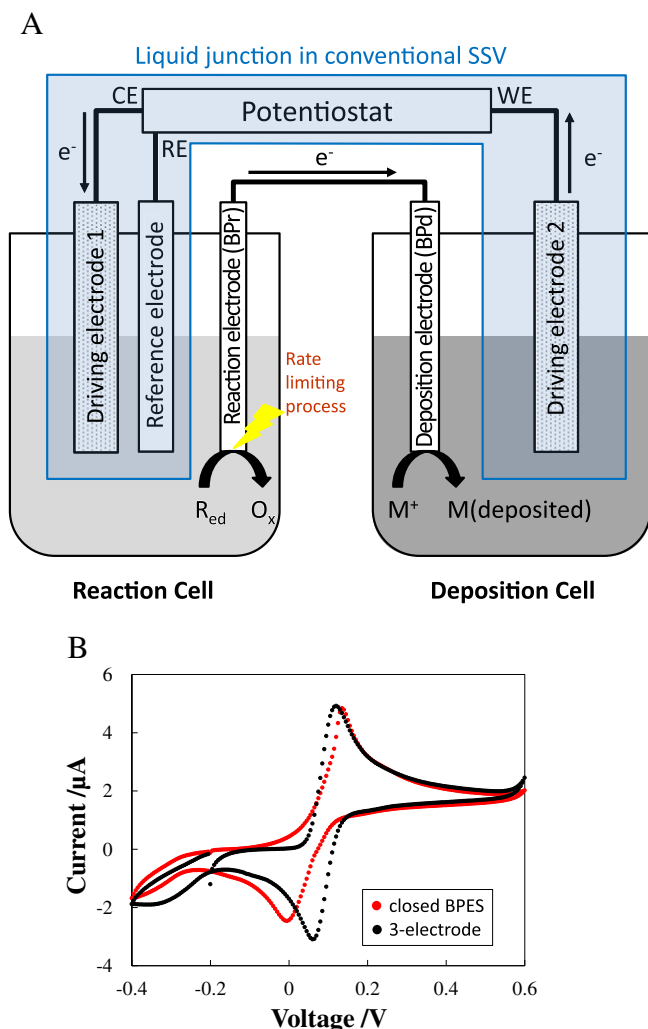
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**Fig. 1.** (A) Schematic illustration showing the basic design of the liquid-junction-free system for SSV. (B) Typical voltammograms obtained in the cBPES (red) and the three-electrode system (black). Au electrodes with 1.6 mm diameter were used for BPr, BPd, and the WE in the three-electrode system. 1.0 mM pAP/100 mM HEPES solution containing 100 mM KCl was used as the reaction solution of BPES and the three-electrode system. 10 mM AgNO<sub>3</sub>/100 mM KNO<sub>3</sub> solution was used as the deposition solution for the BPES. Scan rate was 20 mV/s.

closed bipolar electrode system (cBPES) proposed by Zhang's group [7,8]. The same system was also reported by Girault's group [9], Osakai's group [10] and Dryfe's group [11]. Crooks' group reported the use of a bipolar electrode (BPE) as a sensing platform using metal oxidations [12,13], as well as an alternative system to micro/nanochannel junction for ion transportation [14,15]. However, there are no reports of cBPES used for SSV.

In this study, we propose a liquid-junction-free SSV system using a cBPES. We prove the principle of our system by demonstrating the quantitative detection of *p*-aminophenol (pAP). This is for the future application of this system to the endotoxin sensor which we reported previously using conventional SSV with the combination of oxidation of pAP and reduction of Ag<sup>+</sup> [3]. First, we characterize the cBPES by cyclic voltammetry in order to check the necessary conditions for the quantitative detection of pAP. Then, we demonstrated the quantitative detection of pAP. The successful results indicate that our proposed system is a promising method for the fabrication of compact-type SSV sensors for highly sensitive detection.

## 2. Material and methods

### 2.1. Chemicals and apparatus

Reaction solutions (pAP/HEPES) were prepared by dissolving pAP (Wako Pure Chemical Ind. Ltd., Japan) with 100 mM HEPES (Dojindo Molecular Technologies, Inc., Japan) solution (pH 7.0) containing 100 mM KCl as an electrolyte. Deposition solutions (AgNO<sub>3</sub>/KNO<sub>3</sub>) were prepared by dissolving AgNO<sub>3</sub> with 100 mM KNO<sub>3</sub> solution. All chemicals used were special reagent grade. For the preparation of aqueous solutions, high-purity distilled and deionized water from a Milli-Q filtration system (Millipore Corporation, USA) was used. CompactStat (Ivium Technologies B.V., Netherlands) was used as a potentiostat to perform all electrochemical measurements.

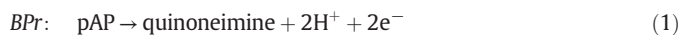
### 2.2. Electrochemical cells

A conventional three-electrode measurement cell was constructed with a Au disk electrode having a diameter of 1.6 mm (BAS Inc., Japan), a Au-sputtered electrode and a Pd sputtered electrode used as WE, CE and RE, respectively. A cBPES for a liquid-junction-free SSV was constructed as shown in Fig. 1A. BPr and BPd were Au disk electrodes. A Au-sputtered glass substrate (2 mm × 10 mm) and a Pd-sputtered glass substrate (2 mm × 10 mm) in the reaction cell were used as driving electrode connected to the CE connector of a potentiostat and a RE, respectively. In a deposition cell, a Ag plate (5 mm × 15 mm) was inserted as another driving electrode which connected to the WE connector on the potentiostat.

## 3. Results and discussion

### 3.1. Voltammetric response of liquid-junction-free system for SSV

First, we characterized the electrochemical properties of the liquid-junction-free SSV system using cyclic voltammetry. The reaction cell shown in Fig. 1A was filled with 1.0 mM pAP/HEPES, and the deposition cell was filled with 10 mM AgNO<sub>3</sub>/KNO<sub>3</sub>. The concentration of AgNO<sub>3</sub> was set to 10 times higher than the concentration of pAP, so that the pAP redox reaction at the BPr was rate limiting. We scanned the voltage of the Ag driving electrode in the deposition cell versus the Pd RE in the reaction cell and recorded the current response. As a comparison, a conventional three-electrode measurement was performed in 1.0 mM pAP/HEPES. Fig. 1B shows typical voltammograms obtained in the cBPES and the three-electrode system at a scan rate of 20 mV/s. When the potential was scanned to the positive direction from −0.2 V, an increase in the oxidation current was observed, making an oxidation peak at 0.14 V. When the oxidation current was observed, the oxidation of silver occurred at the driving electrode (used as a WE) in the deposition cell, whereas the reductive reaction occurred at the other driving electrode (used as a CE) in the reaction cell. At the same time, reactions (1) and (2) were considered to occur at the BPr and BPd, respectively.



Because of these reactions, electrons passed through the BPES, as shown in Fig. 1A. After the potential application was reversed to the negative direction at 0.6 V, the oxidation current gradually decreased and converted to a reduction current, leading to a reduction peak at −0.015 V. When the reduction current was observed, a reversed reaction occurred at each electrode. The voltammogram of the cBPES showed a very similar curve to that of the conventional three-electrode measurement. This

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