Improvement Strategies of Coulometric Microdevice Based on Metallization Principle

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Abstract. Microdevice based on metallization principle and coulometry analysis gave a potential for analyte detection (molecules, protein) in a small volume. In previous device, the structure was constructed with a liquid junction and two separated flow channels; one flow channel for the oxidation of analyte and another flow channel for metal deposition. In this work, the liquid junction was replaced with a metal junction or using a voltage source to promote the redox reactions simultaneously. These strategies give the flexibility in controlling the potentials of the electrodes during the metallization. Enhanced deposition of metal was obtained by increasing the potential difference between the solutions from the two flow channels.

1. Introduction

Development of lab-on-chip (LOC) for biological and chemical analysis have been steadily increased within two decades. In chemical studies, lab-on-chip has important features, such as reducing the reagents consumption and rapid detection due to the smaller scale of the reaction chamber. Careful selection of the transducer is important when LOC want to be deployed for on-site measurement. Typical LOC for sensing purpose has been developed depend on its transducers, for example electrochemical-based, mechanical-based, or optical based sensor. Comparing the transducers used for developing the sensors, electrochemical-based sensors have easier instrumental setup for on-site detection.

In our previous work, a coulometric microdevice for the determination of H$_2$O$_2$ in a liquid plug was developed and used to detect the protein in a plug-based sample [1]. It was demonstrated that H$_2$O$_2$ can be collected more rapidly and efficiently in the restricted space. The system was based on simultaneous oxidation of the analyte and reduction of metal ion which occurred on a single electrode. Both reactions occurred separately at a mixed potential condition on the electrodes in different flow channels with liquid junction.

Such concept is similar with metallization; a process commonly found in metal corrosion. Mixed potential occurs when the anodic current and the cathodic current from different redox reactions are equal [2]. Using this method, the information of analyte in one flow channel can be analyzed from the amount of deposited metal in another flow channel (Figure 1A). The amount of deposited metal was measured using coulometry. In this study, improvement of the coulometric device was studied by replacing the liquid junction with a metal wire or a voltage source to promote an increased in the number of deposited metals by shifting the electrode potentials (Figure 1B).
2. Experimental Section

2.1. Materials
These reagents were used for the experiments: Glass wafers (no. 7740, 3 inch, 500 μm thick) from Corning; photoresist S-1818G and SU-8 25 from MicroChem; potassium chloride (KCl), hydrogen peroxide (H₂O₂), zinc chloride (ZnCl₂), ammonium chloride (NH₄Cl₂), nickel (II) sulfate hexahydrate (NiSO₄.6H₂O), nickel (II) chloride hexahydrate (NiCl₂.6H₂O), trisodium citrate dehydrate (C₆H₅Na₃O₇.2H₂O), silver nitrate (AgNO₃), potassium nitrate (KNO₃), and phosphate buffered saline (PBS; pH 7.4) from Wako Pure Chemical Industries; PVA-SbQ from Toyo Gosei; silver wire (diameter: 1.0 mm) from Nilaco Corporation.

2.2. Device Fabrication
Thin-film electrodes were formed on a glass substrate by sputter deposition. The structure of the fluidic channel was created with PDMS by replica molding using mold patterns of the thick-film photoresist (SU-8 25). The PDMS substrate was stacked on the glass substrate. The device has two flow channels, A and B, where the oxidation and reduction reactions occur separately. The flow channels were 70 μm high and 600 μm wide. An array of platinum electrodes, 10 μm wide and 130 μm interelectrode distances from edge to edge, was formed in flow channel A. In flow channel B, the platinum working electrode had 26 pinholes, 10 μm diameter, formed using the positive photoresist as an insulating layer. A Ag/AgCl reference electrode (3 pinholes) and a platinum auxiliary electrode were also formed in flow channel B.

For fabricating the reference electrode, the silver electrode was immersed in a 0.1 M KCl solution along with commercial Ag/AgCl reference electrode and a platinum auxiliary electrode. For the formation of the liquid junction, PVA-SbQ was mixed with a 0.2 M KCl solution (1:1 weight ratio). The mixture was injected into the liquid junction compartment (diameter: 2 mm) and was exposed to ultraviolet light for 1 min to be cured. An open chamber (diameter: 3 mm) to insert one-end of the silver wire was formed on the left portion of flow channel. Figure 2 shows the fabricated device with metal wire connecting two flow channels.
2.3. Measurement of the electrode potential
To check the change of electrode potentials ($\Delta \varphi_1$ and $\Delta \varphi_2$) measured with respect to solution, we measure the electrode potentials with respect to a commercial reference electrode (Figure 3A). The latter potentials will be referred to as $\Delta \varphi_1$ and $\Delta \varphi_2$ to differentiate them from $\Delta \varphi_1$ and $\Delta \varphi_2$. In the first case, working electrode potential in flow channel A with respect to a commercial reference electrode was measured. A 10 $\mu$M H$_2$O$_2$ solution (10 $\mu$L) was injected into flow channel A. A 0.1 M KCl solution was injected into the electrolyte compartment in flow channel B (left side of the liquid junction). A 1.0 M AgNO$_3$ solution was injected into flow channel B (right side of the liquid junction). The two flow channels then connected by the Ag/AgCl wire. A commercial Ag/AgCl reference electrode was inserted into the right inlet of the flow channel A and connected to the reference electrode of potentiostat.

2.4. Coulometry procedure when using modified metal wire
After the formation of electrolyte gel of PVA-SbQ in the liquid junction compartment of flow channel B, a H$_2$O$_2$ solution (volume: 10 $\mu$L; concentration: 10 $\mu$M) containing KCl was introduced into flow channel A and 0.1 M KCl solution were injected into the electrolyte compartment of flow channel B. Next, two sides of the silver wire were inserted in flow channels A and B. Then, a 1.0 M AgNO$_3$ solution was injected into flow channel B and silver was deposited. The solutions were flushed, and the flow channels were washed with pure water. Finally, a 0.1 M KCl solution was injected into flow channel B and coulometry was conducted by applying +0.7 V to the working electrode with respect to the on-chip Ag/AgCl reference electrode.

The procedure for coulometry for metal junction modified with nickel or zinc is similar. In this case, however, one end of the silver wire was modified with nickel or zinc. Figure 3B shows the setup of the experiment and the location of the silver wire.

2.5. Coulometry procedure when using voltage source
After the formation of electrolyte gel in the liquid junction compartment of flow channel B, H$_2$O$_2$ containing KCl was introduced into flow channel A and 0.1 M KCl solution were injected into the electrolyte compartment of flow channel B. Next, a Ag/AgCl wire was inserted into the flow channel A (left inlet) and was connected to the working electrode terminal of the potentiostat. Another Ag/AgCl wire was inserted into the 0.1 M KCl compartment of flow channel B and was connected to the reference electrode terminal of the potentiostat. A 1.0 M AgNO$_3$ solution was then injected into flow channel B, and silver deposition was started by applying a potential for a predetermined time (Figure 3C). The solutions were flushed, and the flow channels were washed with pure water. Finally, a 0.1 M KCl
solution was injected in flow channel B and coulometry was conducted by applying +0.7 V with respect to on-chip Ag/AgCl reference electrode of the device.

![Diagram](image)

**Figure 3.** (A) Setup for measuring the electrode potential in flow channel A and in flow channel B. (B) Coulometry procedure by replacing one-end of the wire with different metal. (C) Simplified schematic in depositing metal by using a voltage source. The flows of electron and current are shown.

3. Results and discussion
There are two methods tested to check the strategies of improving the sensitivity of the device based on metallization principle. In the first method, a one-end of the wire connected to flow channel B was
replaced with nickel or zinc and another end was maintained as Ag/AgCl. In the second method, a potential difference was applied between the two flow channels through silver wires with Ag/AgCl at the ends using a voltage source.

3.1. Shifting mixed potential by modifying the metal junction

From this experiment, the mixed potential can be shifted to increase the amount of deposited silver by modifying one end of the metal wire with another metal to obtain a higher electrode potential difference than that in the previous method. When both sides of the wire are Ag/AgCl electrodes, the range of the potential difference that can be adjusted is limited. However, by replacing the AgCl layer with zinc or nickel, the potential difference will be larger, and the oxidation and reduction reactions can be enhanced.

Modifying one end of the silver wire with zinc gave a much higher response than with AgCl and nickel (Figure 4). The coulometric response signals of zinc-modified wire are typically unsaturated within a short time as in the case of typical signals in coulometry coupled with silver metallization. It is considered that a portion of deposited silver was remained on the pinholes working electrode in flow channel B. Although the difference between $\Delta \varphi_1$ and $\Delta \varphi_2$ was much increased in the case of using zinc and giving a high output charge, controlling the value of $\Delta \varphi_1$ and $\Delta \varphi_2$ by careful selection of the appropriate metal to be deposited is still impractical and not preferable (Figure 5).

![Figure 4](image)

**Figure 4.** Electrode potential measured on the working electrode in flow channel A and in flow channel B.

3.2. Shifting mixed potential by applying the external voltage source

In this experiment, the potential of the platinum electrodes in flow channel A and B were shifted by applying a potential difference between flow channel A with respect to the flow channel B (Figure 3.8A). In this case, when a negative voltage is applied to the Ag/AgCl wire placed in the flow channel A (acts as a working electrode) with respect to the Ag/AgCl wire placed in KCl compartment (acts as a reference electrode), the electrons will move from the electrode of flow channel A to the electrode of flow channel B. As a result, silver is deposited on the working electrode in flow channel B. By increasing the applied voltage from $-0.1$ to $-0.6$ V, the charge steadily increased (Figure 6). However, when higher potential was applied, it was difficult to dissolve the deposited silver later in the coulometric measurement due to the huge amount of metal deposited on the pinhole working electrodes. Such strategy can be tested for more sensitive detection of H$_2$O$_2$ by selecting $-0.6$ V. However, exact potential where the metal deposition still can be used need to be investigated in future study.
Figure 5. Coulometry results of different modified metal wire: green (zinc), red (nickel), and blue (AgCl).

Figure 6. Coulometry results when using voltage source of different potential range from −0.1 V to −0.6 V.

Such approach of detecting H₂O₂ using metallization principle was unique. Typically, detections of H₂O₂ were conducted directly on the working electrode of the chip using the scheme of three-electrode system. Highly sensitive detections were mostly achieved by incorporating nanomaterials on the working electrode [3, 4]. In this work, the approach on maximizing the detection of H₂O₂ was obtained by collecting the deposited metal through mixed potential mechanism. Using this, incorporating nanomaterials on the working electrode may be eliminated to achieve highly sensitive detection. Although the schematic of metallization was not exactly same with common metal corrosion in nature where the reaction of oxidation and reduction occurred on the same reaction area/chamber, such advantage of transferring the information of analyte through other form (collecting the deposited metal) may benefit the future research on H₂O₂ detection methods.

4. Conclusion
In this work, we introduced methods for controlling the amount of deposited silver in coulometry coupled with metallization. Methods for obtaining a high generating current were investigated in this chapter. In the first method, changing one end of the metal junction located in the electrolyte compartment was selected to obtain a larger electrode potentials difference. Although the difference has increased, this strategy still impractical and relatively difficult to control the amount of deposited silver. The last method was found to be simpler. The metal wire that connecting flow channel A and B was replaced with two wires connected to the external voltage source. The amount of deposited silver could be controlled easier by selecting the preferable applied voltage. Such system successfully shows the flexibility to control the redox reaction occurred in another part of the electrode.

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