

ION-SELECTIVE MEMBRANE FORMED IN A MICROFLUIDIC CHIP UTILIZING SURFACE TENSION FORCE FOR HIGH SENSITIVE AMMONIA ION SENSING

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ABSTRACT

This research presents a novel method to produce successive polymeric ion-selective membrane (ISM) embedded in a microfluidic chip with electrochemical electrodes for detecting ammonia ions. The ISM was formed inside the microchannel utilizing a simple flow-through forming technique. Surface tension force on microstructures is used to trap trace amount of polymer liquid doped with ammonia ionophores and form the ion-selective membrane after curing. Series of ion selective membrane with the thickness of around 50 μm can be formed in the microfluidic chip. Due to thinner thickness and higher surface-area of the formed membranes, the sensing performance can be greatly enhanced due to the faster ion diffusion through the ISM. Results show that the developed microchip has a good linear response for detecting ammonia ion of the concentration between 0.0001 and 1000 ppm ($R^2 \sim 0.9689$) and the limit of detection is measured to be as low as 0.1 ppb. The time response for measuring 0.01 ppm of ammonia ion is only 4 s (95% standard) which is much faster than that of using typical commercial ISE products (\sim minutes). The developed microchip with integrated ion-selective membrane provides a low-cost yet high performance way for continuous detecting ammonia ions.

KEYWORDS: ion-selective membrane, microfluidic chip, ammonia ion, ionophores, surface tension force

INTRODUCTION

Electrochemical detection of redox reactions is one of the most promising techniques for analyzing specific ions in solution. The redox potentials and currents of the analytes can be electrochemically measured. However, this approach may suffer from the interferences with similar redox potentials and results in false signals. To overcome this problem, ion selective electrode for filtering out the undesired ions and leaving only the target ions for electrochemical detections has been reported. Ion selective electrode (ISE) is typically composed of a standard electrochemical electrode that covered with ion selective membrane for detecting specific ion samples in solutions. This technique has been applied in food industry, waste water or environment pollutant monitoring. The first ion-selective membrane electrode using a liquid ion exchanger was reported by Rose in 1967 [1]. A device used aqueous-organic interfaces to extract ions from samples using the ion permeable membrane for specific ions [2]. Inspired by this work, ion selective membrane has become an important detection scheme in electrochemical detections. In recent years, various methods have been developed to measure the membrane potential by the electrochemical detection of the probe ions across the membrane [3]. The relationship between the sample concentration ratio and membrane potential can be described by Nernst equation. Microfluidic devices integrated with polymeric or liquid membrane electrodes for ion-selective detections have attracted researchers in the field of MicorTAS. For example, Manz *et. al* presented the concept for attaching a single ISE membrane inside a micro-channel depend for Ba^+ detection [4]. However, the sensing performance of the device is an issue due to the relative thick membrane. In order to improve the sensing performance of an ISE microchip, a thinner membrane with larger diffusion area is essential. Recently, Hisamoto *et. al* reported a chemicofunctional membrane formed at the contact interface of two reactive solutions in a microchip [5]. However, this process relies on a precise control for the two reactive solutions; otherwise the membrane formation could be unstable or discontinuous. Therefore, this study reports a simple and reliable method to form ion-selective membrane within a microfluidic chip utilizing the high surface tension force of microstructures.

EXPERIMENT

Figure 1 illustrated the concept for the forming mechanism of the proposed ion-selective membrane in an ISE microchip. The injected PVC solution can be pinched at the center of the microchannel due to the neighboring air flows induced by the vacuum suction. PVC solution doped with ionophores is then self-attaching onto the designed microstructures and forms a thin PVC layer at the center of microchip by the assistance of surface tension force and vacuum suction. Since the thickness of the formed membrane is only depend on the vacuum suction, the dimension of the microstructure, material property of the microchannel and the surface tension of the PVC solution. A series of ion selective membranes with uniform thickness can be formed in the microchannel with this simple approach. Figure 2 shows the fabrication process of the proposed ISE microchip for electrochemical detection of ammonia ions. The fabrication process is based on a standard PDMS replication technique for producing the microfluidic channel (Fig. 2A) and a standard electrode pattern technology for producing the electrodes for electrochemical detection (Fig. 2B). The Ag/AgCl reference electrode was then produced by a controlled chlorination process of the sputtered silver electrode. (Fig. 2C) Note that chlorination was achieved by immersing the patterned substrate in a 0.1 M HCl

solution with the application of a constant electrical potential of 1.5 V for 10 second. The PDMS replica and the substrate with EC detecting electrode was treated with oxygen plasma and bonded together to seal the microfluidic channel. (Fig. 2D~2E) Finally, the PVC solution was filled into the microchannel and the membranes were formed on the microstructures utilizing the surface tension force. (Fig. 2F) Figure 3 shows a photo image of the ISE microchip after assembly and an SEM image for the surface morphology of the formed ion-selective membrane. The microchannels separated by the ISE membrane are for sample solution feed-through and electrolyte solution replacement for EC detection of ammonia ions, respectively. The EC electrodes are with 2.0 mm in width and 2.0 mm in pitch. (Fig. 3A) Figure 3B shows the SEM image for the close-up view of the ion-selective membrane formed inside the microstructure. A continuous and dense packed PVC membrane was successfully formed. Figure 4 shows the experimental setup for evaluating the sensing performance of the produced microchip device. The sample solution and the electrolyte were injected with syringe pumps. The sample solution flows through the ISE contact area then the ammonia ions diffuse into the ISE sensing chamber for potential state measurement with the EC electrodes. More importantly, the developed chip is easy to renew the electrolyte in the microchip for obtain a stable and refreshable measurement for electrochemical detection.

RESULTS AND DISCUSSION

Figure 5A shows the cross-section view of multiple ion-channels where the ion selective membranes were formed (Fig. 5B). Results show that the surface tension force successfully trapped constant amount of ionophore doped PVC solution and formed the ion selective membrane. The sensing performance of the produced ISE microfluidic device was evaluated by cyclic voltammetry measurement of ammonia ion solutions of different concentrations. Figure 6 shows the cyclic voltammogram for detecting NH_4Cl (aq) with the concentration range from 0.01 to 1000 ppm. Significant redox signals confirmed that the good sensing performance of the developed microchip integrated with ISM. Results also indicate that the measured current responses increased with the increasing concentration. Moreover, the significant redox signals were symmetric at the potentials of ± 0.28 V also indicated the nice redox reaction on the EC electrodes. Figure 7 presents the measured calibration curve for detecting ammonia ion in the concentration range of 10^{-4} to 10^3 ppm. The developed ISE chip exhibited a detection limit of 0.1 ppb which is much lower than that of commercial ISE products of around 0.1 ppm. The thinner thickness and higher surface-area of the formed ISM significantly improve the sensing performance of the ISE microchip. The nice linearity confirmed that high performance electrochemical detection can be achieved using the ISE microfluidic system. Figure 8 presents the time response for detecting NH_4Cl (aq) of various concentrations using the developed ISE microchip. Note that the concentrations for NH_4Cl was in the range of 0.01 to 1.0 ppm and the channel were refreshed by flushing new sample solution in the microchannel after each test run. Results shows that the ISE sensor reached 95% of the current response in seconds which is also faster than that of commercial ISE (around tens seconds). The developed microchip device provides a low-cost and high performance way for detecting NH_4^+ in $\mu\text{-TAS}$. The ISE sensor also presented a simple method to fabricate the NH_4^+ selective membrane in a sealed microfluidic device.

CONCLUSIONS

This study has successfully developed a simple and low cost process to produce ISE microchip integrated with the ion selective membrane between the microstructures. Surface tension force and the designed geometry of the microstructures made the formed ion membrane thin and had high specific area for ion diffusion. This approach will be improve the field of automated techniques for assembling the NH_4^+ sensor. Results show the developed ISE has good sensing performance for detecting NH_4^+ in the concentration range from 10^{-4} to 10^3 ppm. The ISE chip also shows rapid response of around 4 s (95% standard) for measuring 0.01 ppm of ammonia ion, which is much faster than that of using commercial ISE products. Furthermore, the ion selective membrane has a possibility for the multiple-analyte detection by utilizing the ion selective membrane which is doped with different enzyme. The microchip device provides an excellent approach for developing new ion selective sensors with different ion detection capability.

ACKNOWLEDGEMENTS

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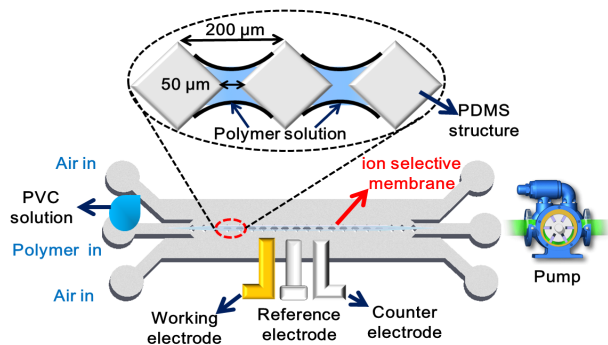


Figure 1. Concept of the membrane forming technique utilizing surface tension force.

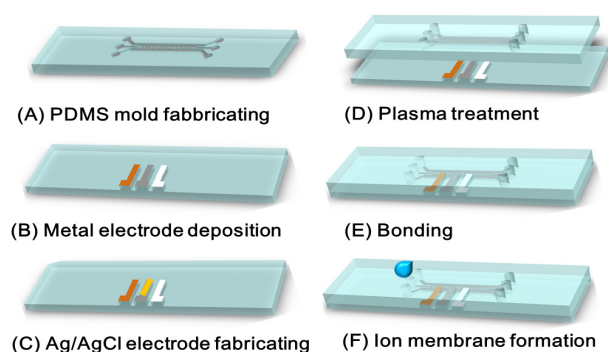


Figure 2. A simplified fabrication process for producing the microfluidic chip integrated with ammonium ion selective membrane.

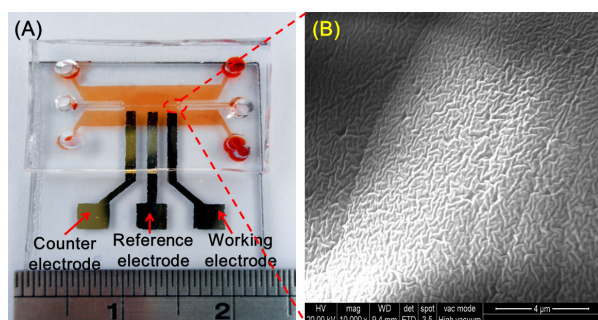


Figure 3. (A) Photo image of the microfluidic chip after assembly. (B) SEM image showing the formed membrane surface ($\times 10,000$).

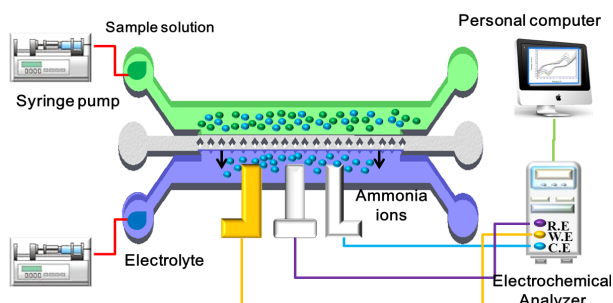


Figure 4. Experimental setup for testing the microchip with ion-selective membrane.

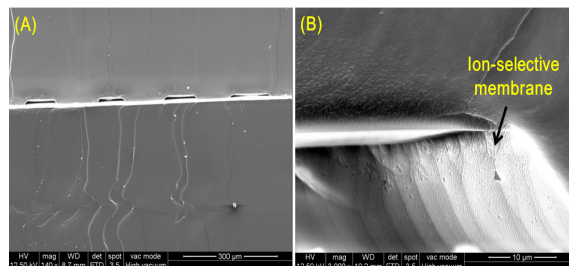


Figure 5. (A) Cross section views of the ion-channel structure. (B) The formed ion membrane inside the ion-channel.

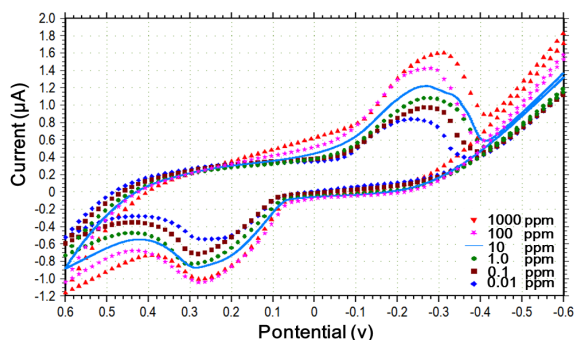


Figure 6. Cyclic voltammogram for sensing different concentrations of NH_4Cl solutions with the ISE microfluidic device.

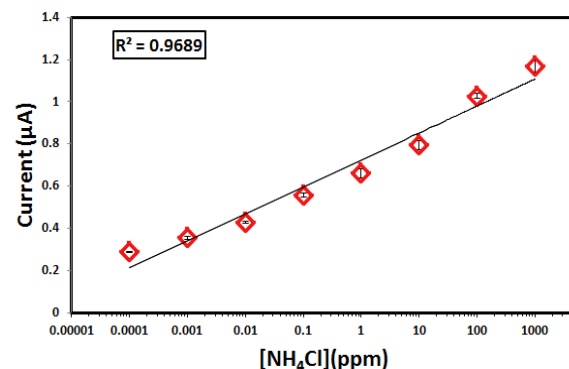


Figure 7. Current response versus the concentration of NH_4Cl (aq).

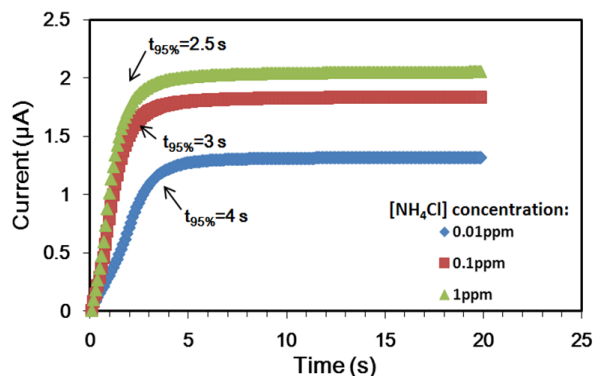


Figure 8. Time response of the microchip under various concentrations of NH_4Cl (aq).