Fabrication of an All-Solid-State Ammonium Ion-Selective Electrode by a Two-Step Process Using Cyclic Voltammetry †

Abdelmohsen Benoudjit, Mohd. Firdaus Abd-Wahab and Wan Wardatul Amani Wan Salim *

Department of Biotechnology Engineering, Faculty of Engineering, International Islamic University Malaysia, Gombak, Kuala Lumpur 50728, Malaysia; benoudjit.ab@gmail.com (A.B.); firdaus@iium.edu.my (M.F.A.-W.)

* Correspondence: asalim@iium.edu.my; Tel.: +60-16-444-5364
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Abstract: Ammonium ion (NH4+) is one of the indicators of water quality. High ammonium concentration [NH4+] in water can cause eutrophication, affect aquatic biota, and cause cell death in the central nervous system of human beings. However, current ion-selective electrodes used for water-quality monitoring are bulky, require frequent calibration owing to membrane fouling, and cannot be integrated into mobile sensor platforms. We fabricated an all-solid-state ion-selective electrode (AS-NISE) for ammonium ion using a two-step process. The first step is electropolymerization deposition on the electrode using a solution of 3,4-ethylenedioxythiophene (EDOT), sodium polystyrene sulfonate (NaPSS), and lithium perchlorate (LiCLO4), resulting in a solid-state transducer on screen-printed carbon electrodes (SPCEs), and the second is electropolymerization deposition of EDOT, NaPSS, and o-phenylenediamine (o-PD) as an ammonium ion–selective membrane (NISM) on top of the transducer. The electropolymerization deposition of the transducer and the NISM were simply achieved by cyclic voltammetry (CV) with potential from 0.0 V to 0.8 V and 50 mVs⁻¹ scan rates. The fabricated AS-NISE can detect [NH4+] as low as 5.7×10⁻⁵ M with a slope of 61.9 mV/decade (R²>0.99) and a linear range from 10⁻³ M to 1 M. These preliminary results provide an initial insight into the applicability of the simple two-steps fabrication process of NH4+ ISEs for scaling-up purposes with the ability for miniaturization and integration into a mobile sensor platform.

Keywords: all-solid-state ion-selective electrode; electropolymerization; ammonium ion; cyclic voltammetry; EDOT

1. Introduction

Ammonium ions (NH₄⁺) can present as a form of dissolved nitrogen generated by heterotrophic bacteria in water bodies. Ammonium can be a primary nitrogenous end product from the decomposition of N-organic compounds such as proteins. The concentration of NH₄⁺ can increase rapidly in water as these ions are photosynthetically assimilated, stored, transformed, and excreted by aquatic organisms. Therefore, NH₄⁺ concentrations can indicate zones with high biogeochemical activity [1], and real-time and continuous monitoring of ammonium using sensors is required at such places.

Among the ion sensors, all-solid-state ion-selective electrodes (AS-ISEs) for NH₄⁺ are flexible, provide in-situ and real-time measurement, and can be miniaturized for integration into mobile platforms [2–5]. Ion-selective membranes (ISMs) as the sensing element in AS-ISE has been a crucial part in the fabrication process that determine sensors selectivity [6]. Traditionally, ISM is fabricated using a cocktail of materials consisting of pyrometers, plasticizers, ionophores, and stabilizers that
are drop-cast onto the working electrode [6–8]. However, the drop-casting method suffers from weak adhesion of the drop-casted material to the electrode surface and shorter sensor lifetime [3,9], which could not be suitable in situations requiring continuous measurement in aqueous media.

Conducting polymers (CPs) have been used for the fabrication of AS-ISE due to their favorable ion to electron conductivity property [10,11], and it can be electropolymerized and deposited on electrode surfaces [9,12], which could enhance the life-time of the AS-ISE. A study showed that a conductive polymer Poly (o-phenylenediamine) (PoPD) was successfully electropolymerized and deposited as ISM for NH4+ detection and it is contributed to the lifetime of the sensor [3]. However, more studies are needed for miniaturization and the scaling up purpose.

The aim of this work is to investigate the performance of the all-solid-state ammonium ion-selective electrode (AS-NISE) fabricated using a two-step process. First is electropolymerization deposition (EPD) of the PEDOT:PSS transducer, and the second is EPD of PoPD-PEDOT:PSS onto a screen-printed carbon electrode as an ion-selective membrane.

2. Materials and Methods

2.1. Materials

Electrochemical characterization was performed using a portable PocketSTAT™ (IVIUM Technologies, Eindhoven, The Netherlands). A compatible voltammetry cell and screen-printed electrodes (SPCEs) was purchased from PINE Research Instruments, Grove City, PA, USA. The working electrode (WE) diameter is two millimeters. Monomer 3,4-ethylenedioxythiophene (EDOT) was purchased from Apical Scientific, Seri Kembangan, Selangor, Malaysia. Poly(sodium 4-styrenesulfonate) solution (NaPSS), lithium perchlorate powder (LiClO4), and potassium ferricyanide (K₃[Fe(CN)₆]) were purchased from Sigma-Aldrich, St. Louis, MO, USA. Furthermore, o-phenylenediamine (o-PD) and ammonium chloride were purchased from Santa Cruz Biotechnology, Dallas, Texas, USA. Deionized (DI) water was used throughout the experiments. All measurements were performed in ambient conditions at room temperatures of 25 to 28 °C and humidity of 59% to 65%.

2.2. Fabrication of All-Solid-State Ammonium Ion–Selective Electrode (AS-NISE)

Screen-printed carbon electrodes (SPCEs) were activated using repetitive cyclic voltammetry (CV) for three cycles in 0.1 N H₂SO₄ at extreme anodic and cathodic potentials of 2.5 to −2.5 V and a scan rate of 100 mV/s [13]. The activated SPCEs were rinsed in DI water and left to dry for 24 hours in ambient conditions. The fabrication process of AS-NISE involves two steps (Figure 1). The first step is the electropolymerization deposition (EPD) by cyclic voltammetry (CV) of a poly (3,4-ethylenedioxythiophene: Poly (styrenesulfonate) (PEDOT:PSS) transducer onto the WEs of SPCEs with a potential of 0 to 0.8 V, and a scan rate of 50 mV/s for five cycles in 0.5 ml EDOT, 1 ml NaPSS, and 13.5 ml LiClO₄ (0.1 M). The modified electrode was washed with deionized water and left to air dry at ambient temperature. During the second step, a mixture of EDOT, NaPSS, and o-PD was deposited by a CV method onto the PEDOT:PSS transducer to act as an ammonium ion–selective membrane (NISM). The CV was performed with a potential of 0 to 0.8 V and a scan rate of 50 mV/s for five cycles of scanning in the previous transducer solution containing 0.130 g o-phenylenediamine solubilized by 2 ml HCl (1 M). The fabricated all-solid-state ammonium ion–selective electrode (AS-NISE) was rinsed carefully with DI water and activated in 10⁻³ M NH₄Cl for six hours before use.
Figure 1. All-solid-state ammonium ion-selective electrode (AS-NISE) for ammonium-ion detection fabricated by electro-polymerization deposition of conductive polymers.

2.3. Characterization of PEDOT:PSS Transducer

Surface morphology of electropolymerized deposited PEDOT:PSS on SPCEs was observed using a scanning electron microscopy (SEM, JSM-IT100, JEOL, JAPAN) available at the Metallography Lab, Faculty of Engineering, IIUM, Kuala Lumpur, Malaysia. The electrodes were coated with gold-palladium particles using the Quorum SC7620 sputter coater. CV was performed using a PocketSTAT™ to evaluate the electron-transfer capabilities of the electropolymerized deposited PEDOT:PSS onto the WE of an SPCE as a transducer by measuring the magnitude of the anodic peak current, peak potential drift, and reversibility behavior. CV was conducted in 0.1 M potassium ferricyanide (K3 Fe (CN)6)/0.5 M KCl solution with a potential window of −0.3 V to +0.7 V and a scan rate of 100 mV/s.

2.4. Potentiometry Measurement

Potentiometry measurement was performed to determine voltage change of AS-NISE toward different ammonium ions concentration [NH4+] ranged from 10⁻⁵, 10⁻⁴, 10⁻³, 10⁻², 10⁻¹, and 1 M. The voltage was measured at a current range of 100 μA while sequentially adding 0.5 ml ammonium chloride (NH4Cl). SPCEs were dipped in 20 ml glass vial that was filled with 10 ml of DI water that was used to obtain baseline measurement. Average voltage between each added concentration was calculated to produce a linear regression of voltage (V) versus log [NH4+] graph. Sensitivity of the AS-NISEs calculated form the slope of linear calibration curve. The detection limit (LOD) and linear range of the AS-NISE were obtained from calibration curve. All measurements were performed in an ambient condition at room temperature.

3. Results

3.1. PEDOT:PSS/SPCE Transducer

Scanning electron microscope (SEM) images show that a PEDOT:PSS-modified electrode has a nano-globular morphology (Figure 2b) instead of the sponge-like morphology of a bare electrode (Figure 2a). The globular structure seen in PEDOT:PSS/SPCE confirmed the deposition of PEDOT:PSS onto the WE of the SPCE. The change in the morphology of a PEDOT:PSS/SPCE was validated by CV measurements. At a scan rate of 100 mV/s, the PEDOT:PSS/SPCE (Ipₐ = 482 μA) demonstrated an increase of an oxidation peak current compared to a bare electrode (Ipₐ-Bare = 233 μA). This higher
peak current of PEDOT:PSS/SPCE results from the electrical conductivity of PEDOT:PSS. Furthermore, the difference in CV anodic peak current ($\Delta I_{pa}$) between the bare electrode and PEDOT:PSS/SPCE was calculated from CV graphs (Figures 2c and 2d) to determine the effect of PEDOT:PSS on the peak current. The results showed that the peak current more than doubles ($\Delta I_{pa} = 249 \mu A$). Moreover, a shift of the anodic peak potential from $E_{pa} = 0.33$ V (SPCE) to $E_{pa} = 0.29$ V (PEDOT:PSS/SPCE) was observed. These results suggest that electropolymerized deposition of a PEDOT:PSS transducer improves electron transfer at the WE by increasing the peak current and decreasing the peak potential.

$\textbf{Figure 2.}$ (a) Scanning electron microscope (SEM) image of bare SPCE, (b) SEM image of the PEDOT:PSS/SPCE, (c) CV graphs in 0.1 M $K_3[Fe(CN)_6]$, and 0.5 M KCl for bare SPCE and PEDOT:PSS/SPCE via EPD techniques at a scan rate of 100 mV/s, and (d) PEDOT:PSS/SPCE at various scan rates (V/s) with linear regression between the peak current (Ip) and the square root of the scan rate (mV1/2).

3.2. Calibration Curve

Figure 3a and Figure 3b shows potentiometry measurements and calibration profile of the voltage changes versus log [NH$_4^+$] for PEDOT:PSS/SPCEs and NISM-PEDOT:PSS/SPCEs. In this study, we tested [NH$_4^+$], which ranged from $10^{-5}$ to 1 M NH$_4$Cl. The results showed a linear relationship between voltage and [NH$_4^+$] added for both electrodes: 75.8 mV/decade for PEDOT:PSS/SPCE, which is a super theoretical Nernst value that exceeds the theoretical Nernst value of 59.16 mV/decade [7]. However, NISM-PEDOT:PSS/SPCEs reported Nernst value of 61.9 mV/decade that are closer to the theoretical value. NISM-PEDOT:PSS/SPCEs reached a detection limit of $5.7 \times 10^{-5}$ M, and a linear range of $10^{-3}$ to 1 M. The slope of a graph indicates the sensitivity of a sensor. A high slope means higher sensitivity. In this study, PEDOT:PSS/SPCEs showed the highest slope
compared to NISM-PEDOT:PSS/SPCEs. However, the absence of NISM in PEDOT:PSS/SPCEs can lead to low ion selectivity.

Figure 3. All-solid-state ammonium ion–selective electrode (AS-NISE) characterization. (a) Chronopotentiometry measurements and (b) calibration curve.

4. Conclusions

A NISM-PEDOT:PSS/SPCE for NH$_4^+$ quantification was fabricated using a two-step process: electropolymerization deposition of the transducer and deposition of the ion-selective membrane. The NISM-PEDOT:PSS/SPCE showed a sensitivity of 61.9 mV/decade, which is a value close to the theoretical Nernst value (59.16 mV/decades). The ammonium sensor exhibited a low detection limit of $5.7 \times 10^{-5}$ M with a linear detection range of $5.7 \times 10^{-5}$ to $4.5 \times 10^{-2}$ M. These preliminary results provide an initial insight into the applicability of the simple two-step fabrication process of AS-NISEs. Future studies are warranted to determine the selectivity and chemical interaction between the components of AS-NISEs. Optimization of the electropolymerization deposition parameters is needed as well to expand this work for scaling-up purposes with the ability for miniaturization and integration to a mobile sensor platform.

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