A STABLE SOLID CONTACT TRANSDUCER AND IONOPHORE-FREE ALL-SOLID-STATE AMMONIUM ION-SELECTIVE ELECTRODE FOR MOBILE SENSOR APPLICATION IN AQUEOUS MEDIA

BY

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ABSTRACT

An all-solid-state ion-selective electrode (AS- NH_4^+ISE) for ammonium-ion-sensing based on stable conductive polymer (CPs) as a solid contact transducer and ionophore-free ion-selective membrane for mobile sensor application was fabricated. Poly(3,4 ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) electropolymerized onto screen-printed carbon electrodes (SPCEs), and screen-printed platinum electrodes (SPPEs) as solid contact transducer was characterized for its morphology and electrochemical performance and was studied for stability – the ability of the sensing solid contact transducer to adhere to the working electrode surface and maintain electrochemical cycle stability. The stability of the solid contact transducer was studied in static measurements condition – a condition where the electrodes are submerged in aqueous solution and not moving, and there is no water flow on the electrode surface when the measurements are taken, and dynamic measurements condition – a condition where an aqueous solution flows across the electrode surface and the sensor is not moving when measurements are taken. Cyclic voltammetry (CV) showed that the electron transfer ability of SPCEs and SPPEs was significantly improved when electropolymerized PEDOT:PSS was used as the transducer. Moreover, the CVs' redox peak current showed that both electrodes could maintain the electrode's mechanical and electrochemical functional integrity for over 30 days. The results suggest that the electropolymerized PEDOT:PSS had good adhesion to SPCEs and SPPEs working electrode surfaces. There was no significant change in the cycle stability curve in PBS, pH 7.1, after 3000 cycles conducted over 12 hours, compared to the initial cycle. Furthermore, no significant change in the cycle stability curve was observed after 30 days of undergoing CV cycles in PBS, pH 7.1, compared to the first day for both electrodes. The results suggest that electrode stability of PEDOT:PSS/SPCEs and PEDOT:PSS/SPPEs was maintained after repetitive CV cycles in aqueous media. After characterisation of solid contact transducer, the PEDOT:PSS/SPCEs were integrated into a sensing cell to investigate the electrochemical behaviour of electropolymerized PEDOT:PSS in dynamic measurement conditions. The results showed that the PEDOT:PSS/SPCEs maintained their peak potential (E_p) and peak current (I_p) after they were exposed to different flow rates of 10, 20, 30 and 40 ml/min. Furthermore, the effect of the flow rates on the E_p and I_p was investigated. The results showed that flow rates range between 0 to 40 ml/min did not affect the E_p and I_p value of the PEDOT:PSS/SPCEs. Finally, o-phenylenediamine (o-PD) as an ammonium ion-selective membrane (ISM) was electropolymerized to poly(o-phenylenediamine) and deposited simultaneously on top of the PEDOT:PSS/SPCEs solid contact transducer to fabricate AS-NH_4^+ISEs. The ISM's electropolymerization deposition was obtained by cyclic voltammetry (CV) with potential from 0.0 V to 0.8 V and a scan rate of 50 mV/s. The fabricated AS-NH_4^+ISEs can detect ammonium ions (NH_4^+) as low as 5.7×10^{-5} M with a slope of 58.49 mV/decade ($R^2 > 0.99$) and a linear detection range from 10^{-3} M to 1 M. These results provide an initial insight into the applicability of the stable PEDOT:PSS/SPCE solid contact transducers for the development of AS-NH_4^+ISEs with high potential for scaling-up purposes and the ability for miniaturization and integration into a mobile sensor platform.

خلاصة البحث

تم تصنيع قطب كهربائي انتقائي للأيونات كامل الحالة الصلبة ($AS-NH_4^+ISEs$) لجس أيونات الأمونيوم بناءً على بوليمر ناقل و ثابت كمحول صلب (CPs) كمحول طاقة اتصال صلب وغشاء انتقائي للأيونات خالٍ من الأيونات لتطبيقات المجسات المحمولة. البولمر الناقل المستعمل هو (3،4-إيثيلين ديوكسي ثيوفين) بولي (الصوديوم 4-ستايرين سلفونات) (PEDOT: PSS) حيث تمت بلمرته كهربائيًا وترسيبه على أقطاب كربونية (SPCEs) ، وأقطاب بلاتينية (SPPEs) ليتم دراسة مورفولوجيته واستقرار أداءه الكهروكيميائي. استقرار الأداء الكهروكيميائي للمحول هو قدرته على الالتصاق الجيد بسطح القطب الكهربي العامل والحفاظ على استقرار دورته الكهروكيميائية لمدة طويلة في محلول مائي. تم دراسة استقرار المحول الصلب في الحالة الثابتة – حالة لا تتحرك فيها الأقطاب الكهربائية، ولا يوجد تدفق للمياه على سطح القطب، والحالة الديناميكية – وهي حالة يتدفق فيها محلول مائي عبر سطح القطب. أظهر قياس الجهد الدوري (CV) في الحالة الثابتة للقطبين الكهربائيين العاملين الكربوني والبلاتيني أن قدرتهما لنقل الإلكترونات قد تحسنت بشكل ملحوظ بعد بلمرة وترسب PEDOT:PSS عليهما. علاوة على ذلك، أظهر قياس الجهد الدوري (CV) أن كلا القطبين يمكن أن يحافظا على السلامة الوظيفية الميكانيكية والكهربائية للقطب لأكثر من 30 يومًا. تشير النتائج إلى أن PEDOT: PSS المبلمر كهربائيًا كان له التصاق جيد بأسطح القطب الكهربائي العامل لـ SPCEs و SPPEs. كما لوحظ هناك تغير طفيف في منحنى استقرار الدورة في محلول PBS درجة الحموضة 7.1 ، بعد 3000 دورة أجريت على مدى 12 ساعة ، مقارنة بالدورة الأولية. علاوة على ذلك، لوحظ تغيير طفيف في منحنى الاستقرار بعد 30 يومًا من خضوعهما لقياس الجهد الدوري (CV) يوميا في محلول PBS ، درجة الحموضة 7.1، مقارنة باليوم الأول لكلا القطبين. أكدت النتائج إلى أن القطبين الكهربائيين PEDOT: PSS / SPCEs و PEDOT: PSS / قد حافظا على استقرارهما بعد قياسات الجهد الدوري (CV) المتكررة في الوسائط المائية. بعد توصيف المحول الصلب المثبت على القطب الكربوني ، تم دمج PEDOT: PSS / SPCEs في غرفة استشعار للتحقيق من اداءه الكهروكيميائى في ظروف القياس الديناميكية. أظهرت النتائج أن PEDOT: PSS / SPCEs حافظ على ذروة فرق الكمون (E_p) وذروة التيار الكهربائي (I_p) بعد تعرضها لمعدلات تدفق مختلفة تبلغ 10 و 20 و 30 و 40 مل / دقيقة. علاوة على ذلك، تم التحقق من تأثير معدلات التدفق على E_p و I_p. أظهرت النتائج أن التدفق الذي يتراوح بين 0 إلى 40 مل / دقيقة لم يؤثر على قيمة E_p و I_p لـ PEDOT: PSS / SPCEs علما ان القياسات اخذت أثناء التدفق لمحلول البوتاسيوم فيروسيانيد. أخيرًا، تمت بلمرة o-phenylenediamine (o-PD) كغشاء انتقائي لأيون الأمونيوم (ISM) إلى poly(o-phenylenediamine) وترسيبه في وقت واحد على المحول الصلب PEDOT: PSS / SPCEs لتصنيع $AS-NH_4^+ISEs$. تمت البلمرة والترسب الكهربائي لـ ISM عن طريق الجهد الدوري (CV) بنافذة فرق كمون من 0.0 فولت إلى 0.8 فولت ومعدل مسح قدره 50 ملي فولت / ثانية. اظهرت النتائج ان القطب الكهربائي الانتقائي لأيونات الأمونيوم كامل الحالة الصلبة $AS-NH_4^+ISEs$ المصنع يمكنه تحسس أيونات الأمونيوم (NH_4^+) بقيمة منخفضة تصل إلى 5.7×10^{-5} مول مع حساسية تصل لـ 58.49 ملي فولت / عقد ($R2 > 0.99$) و مع نطاق كشف خطي من 10^{-3} مول إلى 1 مول توفر هذه النتائج نظرة أولية حول قابلية تطبيق محول الطاقة الثابت PEDOT: PSS / SPCE ذات الحالة الصلبة لتطوير صناعة $AS-NH_4^+ISEs$ بإمكانية عالية والقدرة على التصغير والتكامل في منصة مستشعر متنقل.

APPROVAL PAGE

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DECLARATION

I hereby declare that this thesis is the result of my own investigations, except where otherwise stated. I also declare that it has not been previously or concurrently. submitted as a whole for any other degrees at IIUM or other institutions.

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LIST OF ABBREVIATIONS

CE	Counter electrode
WE	Working electrode
RE	Reference electrode
SPEs	Screen-printed electrodes
SPCEs	Screen-printed carbon electrodes
SPPEs	Screen-printed platinum electrodes
CPs	Conductive polymers
CV	Cyclic voltammetry
EPD	Electropolymerization deposition
DW	Distilled water
DIW	Deionized water
ISE	Ion selective electrode
PIS	Potentiometric ion sensor
AS-ISEs	All-solid-state ion-selective electrodes
AS-NH_4^+ISEs	All-solid-state ammonium ion-selective electrodes
ISM	Ion-selective membrane

LIST OF NOTATIONS

E_p	Peak potential (V)
E_{pa}	Anodic peak potential (V)
E_{pc}	Cathodic peak potential (V)
I_p	Peak current (µA)
I_{pa}	Anodic peak current (µA)
I_{pc}	Cathodic peak current (µA)
ΔI	Current difference (µA)
ΔE_p	Peak-to-peak potential separation (V)
Q	Flow rate (ml/s)
v	Velocity (m/s)
A	Area (m^2)
v_A,	Velocity at point A
v_B	Velocity at point B
A_A	Area at point A
A_B	Area at point B

LIST OF SYMBOLS

CO_2	Carbon dioxide
EDOT	3,4-Ethylenedioxythiophene
H_2SO_4	Sulfuric acid
HCl	Hydrochloric acid
$K_3[Fe(CN)_6]$	Potassium ferricyanide
KCl	Potassium chloride
KH_2PO_4	Monopotassium phosphate and
$LiClO_4$	Lithium perchlorate
Na_2HPO_4	Disodium phosphate
NaCl	Sodium chloride
NH_4^+	Ammonium ion
O_2	Oxygen
o-PD	o-phenylenediamine
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)
Po-PD	Poly(o-phenylenediamine)
PPy	Polypyrrole
PSS	Polystyrenesulfonic acid

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND OF THE STUDY

Ammonium ions (NH_4^+) are one of the indicators of water quality and can be in the 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 NH_4^+ can increase rapidly in water as these ions are photosynthetically assimilated, stored, transformed, and excreted by aquatic organisms (Han L, 1985). Furthermore, high NH_4^+ concentration in natural water can cause eutrophication and result in water algal bloom and red tide releasing the toxin, killing aquatic biota. Large amounts of continuous water consumption with high ammonium content can also cause cell death in the human body's central nervous system (Kan et al., 2016). Therefore, high NH_4^+ concentrations can indicate high biogeochemical activity zones; thus, real-time and continuous ammonium monitoring using sensors is required at such places.

Ion-sensors, ion-selective electrodes (ISE), or potentiometric ion sensors (PIS) form an essential subgroup for electrochemical sensors widely used for ammonium ion sensing (Radomska et al., 2004; Schwarz et al., 2000). However, conventional ISEs have several limitations: complicated maintenance, complex operations, and high costs. Furthermore, ISEs contain liquid as the inner filling solutions that separate the sensing membrane from the inner reference element. The filling solution is sensitive to evaporation, especially when there are changes in the measured solution's temperature or pressure. Therefore, conventional ISEs must be well maintained and used with care and frequent calibration. Moreover, reducing the volume of a measurement sample to a value much lower than the millilitre level is difficult, which poses challenges for sensor miniaturization (Ghosh et al., 2017; Hu et al., 2016). The ISEs are classified into three groups, depending on the nature of the membrane material, which are glass, polymeric or liquid, and crystal or solid (Faridbod et al., 2007).

All-solid-state ion-selective electrodes (AS-ISEs) replace the internal electrolyte filling with a solid ion-to-electron transducer (solid contact transducer) (Bieg et al., 2016). AS-ISEs can be used in next-generation sensor devices due to the ease of integrating AS-ISEs with electronics. Signal stability has been improved, and detection limits were lowered through various research efforts (Hu et al., 2016; Wu et al., 2013). The advancement in screen-printed electrode technology also played a significant role in the research on the application of AS-ISEs in various fields requiring continuous monitoring (Cuartero & Crespo, 2018). Critical components of AS-ISEs are the ion-selective membrane (ISM) and the solid contact transducer, deposited on a conductive electrode made from carbon, platinum, or gold. The ISM's role is to recognize and select the target ion. Simultaneously, the solid contact transducer converts the target-ion concentration to an electrical potential (voltage) measured against a reference electrode (Hu et al., 2016).

An ion-selective membrane (ISM) cocktail consists of four components: a polymeric matrix, an ionophore which is a membrane-active recognition material, a membrane solvent or plasticizer, and ionic additives. The standard composition of an ISM is 33% (w/w) polymeric matrix, 66% (w/w) plasticizer, 1% (w/w) ionophore, and 0.5% (w/w) ionic additives; each component of the ISM depends on the target ion, especially for its ionophore (Faridbod et al., 2008). However, the AS-NH_4^+ISEs can be ionophore-based or ionophore-free (Cuartero et al., 2020). Recent research showed that AS-NH_4^+ISEs without ionophores have the potential for environmental applications, owing to their long lifetime and stability in liquid media (Kan et al., 2016). The o-phenylenediamine (o-PD) is one of the polymers used as an ISM to replace conventional ionophore-based ISMs. The results were insightful and promising due to its sensitivity toward the NH_4^+ and its ease of fabrication through one-step electropolymerization deposition, which could provide ways to scale up the fabrication of AS-ISEs for industrial use (Benoudjit, Abd-Wahab, et al., 2020; Cuartero et al., 2020; Kan et al., 2016).

Conventionally, the solid contact transducer is a conductive polymer (CP) deposited on the electrode surface via drop-casting. However, the drop-casting method suffers from weak adhesion of the drop-casted material to the WE surface, especially when the deployment conditions for measurements are different, which could limit the application of the sensor (Benoudjit et al., 2018; Cuartero & Crespo, 2018). Hence, a CPs as a solid contact transducer with the following favourable characteristics is needed in the fabrication of AS-NH_4^+ISEs for mobile sensor application in aqueous media:

1. displays strong mechanical adhesion to electrode surfaces; and
2. operates with stable cyclic voltammetry (CV) profile after repetitive CV cycles.

Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) is one of the CPs used as the solid contact transducer for AS-ISE development. It is less sensitive to atmospheric gases (O_2 and CO_2) than a polypyrrole (PPy) solid contact transducer (Bobacka, 2006). However, PEDOT:PSS comes with its limitations; the presence of hydrophilic PSS chains in PEDOT:PSS can lead to weak adhesion onto the electrode surface, which results in film degeneration and peeling from the electrode (Wang et al., 2014; Zhang et al., 2015). For this reason, previous research has focused on enhancing PEDOT:PSS's adhesion and water stability to electrodes by adding polyvinyl alcohol (PVA) (Wang et al., 2014), nafion (Wen et al., 2012), or sodium carboxymethyl cellulose as a binding reagent (Li et al., 2015). However, most of the tests conducted on PEDOT:PSS adhesion on electrode surfaces were measured in solution in a typical laboratory setting – static measurements condition in which the electrodes are submerged in measurement solution, the electrodes are not moving, and without water flow on the electrode surface. Moreover, our initial work demonstrated that PEDOT:PSS deposited by electropolymerization deposition technique on screen-printed platinum electrodes (SPPEs) could overcome the problem by enhancing the adhesion PEDOT:PSS to the electrode surface (Benoudjit et al., 2018).

However, few studies have been made on understanding the stability of electropolymerized PEDOT:PSS on screen-printed carbon electrodes (SPCEs) as solid contact transducers for applications in static and dynamic measurements conditions and their applicability for AS-NH_4^+ISEs. Therefore, this work aims to develop a stable AS-NH_4^+ISEs-based on PEDOT:PSS as a solid contact transducer and Po-PD as an ion-selective membrane (ISM) ionophore-free for mobile sensor application in aqueous media.

1.2 PROBLEM STATEMENT

The key components of all-solid-state ammonium ion-selective electrodes (AS-NH_4^+ISEs) are the solid contact transducer and the ion-selective membrane (ISM). The stable performance of the AS-NH_4^+ISEs for prolonged measurements in aqueous media requires a stable solid contact transducer and ISM. However, solid contact transducer and ISM tend to deteriorate in liquid media by losing their electrochemical capabilities and can be easily peeled off from the surface of electrodes after prolonged storage or use in liquid media which lead to unstable sensor performance. Therefore, in this work the poly (o-phenylenediamine) (Po-PD) as an ISM and poly (3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) as solid contact transducer were selected. The poly (o-phenylenediamine) (Po-PD) as an ISM has shown good stability for up to 5 months (Kan et al., 2016), and I have shown such ISM can be fabricated by a one-step process (Benoudjit, Abd-Wahab, et al., 2020). Moreover, my preliminary work on investigating the stability of poly (3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) as solid contact transducer on screen-printed platinum electrodes (SPPEs) (PEDOT:PSS/SPPEs) has shown that PEDOT:PSS/SPPEs possessed good stability in static measurements conditions -in which the electrodes are not moving when measurements are made in aqueous media, and there is no water flow on the electrode surface, and also dynamic conditions, in which an aqueous solution flows across the electrode surface at a fixed flow rate (Benoudjit et al., 2018).

Few studies have been made on understanding the stability of electropolymerized PEDOT:PSS on screen-printed electrodes (SPEs) as solid contact transducer in static and dynamic measurements conditions and its applicability in AS-NH_4^+ISEs. Therefore, this work aims to develop stable AS-NH_4^+ISEs based on electropolymerized PEDOT:PSS as the solid contact transducer on screen-printed carbon electrodes (SPCEs) for the purpose of integration in a mobile sensor platform for prolonged and real time-time measurements in aqueous media. The future end goal is to develop a mobile sensor platform that can be deployed in rivers or coastal areas for water quality monitoring. As NH_4^+ ions play a critical role in the occurrence and