

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

BY

ABDELMOHSEN BENOUDJIT

A thesis submitted in fulfillment of the requirement for the
degree of Doctor of Philosophy (Engineering)

**Kulliyyah of Engineering
International Islamic University Malaysia**

JANUARY 2022

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. البوليمر الناقل المستعمل هو (3,4-إيثيلين ديوكسي ثيوفين) بولي (الصوديوم 4-ستايرين سلفونات) (PEDOT: PSS) حيث تمت بلمرته كهربائياً 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 الكهربائي 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 يوماً. تشير النتائج إلى أن PEDOT: PSS المبلمر كهربائياً كان له التصاق جيد بأسطح القطب الكهربائي العامل ل SPCEs و SPPEs. كما لوحظ هناك تغير طفيف في منحني استقرار الدورة في محلول PBS درجة الحموضة 7.1 ، بعد 3000 دورة أجريت على مدى 12 ساعة ، مقارنة بالدورة الأولى. علاوة على ذلك، لوحظ تغيير طفيف في منحني الاستقرار بعد 30 يوماً من خضوعهما لقياس الجهد الدوري (CV) يومياً في محلول PBS ، درجة الحموضة 7.1 ، مقارنة باليوم الأول لكلا القطبين. أكدت النتائج إلى أن القطبين الكهربائيين PEDOT: PSS / SPCEs و PEDOT: PSS / 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 أداءه الكهروكيميائي 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 ل PEDOT: PSS / SPCEs علما ان القياسات اخذت أثناء التدفق لمحلول البوتاسيوم فيروسيانيد. أخيراً، 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 ل ISM عن طريق الجهد الدوري (CV) بنافذة فرق كمون من 0.0 فولت إلى 0.8 فولت ومعدل مسح قدره 50 ملي فولت / ثانية. أظهرت 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 ل 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


The thesis of Abdelmohsen Benoudjit has been approved by the following:




Wan Wardatul Amani Wan Salim
Supervisor



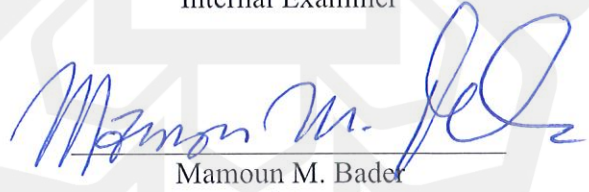
Mohd. Firdaus Bin Abd Wahab
Co-Supervisor



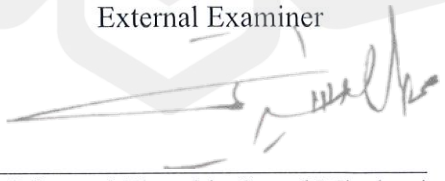
Nassereldeen Ahmed Kabbashi
Co-Supervisor



Anis Nurashikin Nordin
Internal Examiner



Mamoun M. Bader
External Examiner



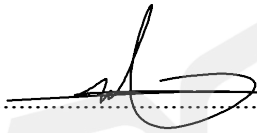
Mohamed Elwathig Saeed Mirghani
Chairman

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.

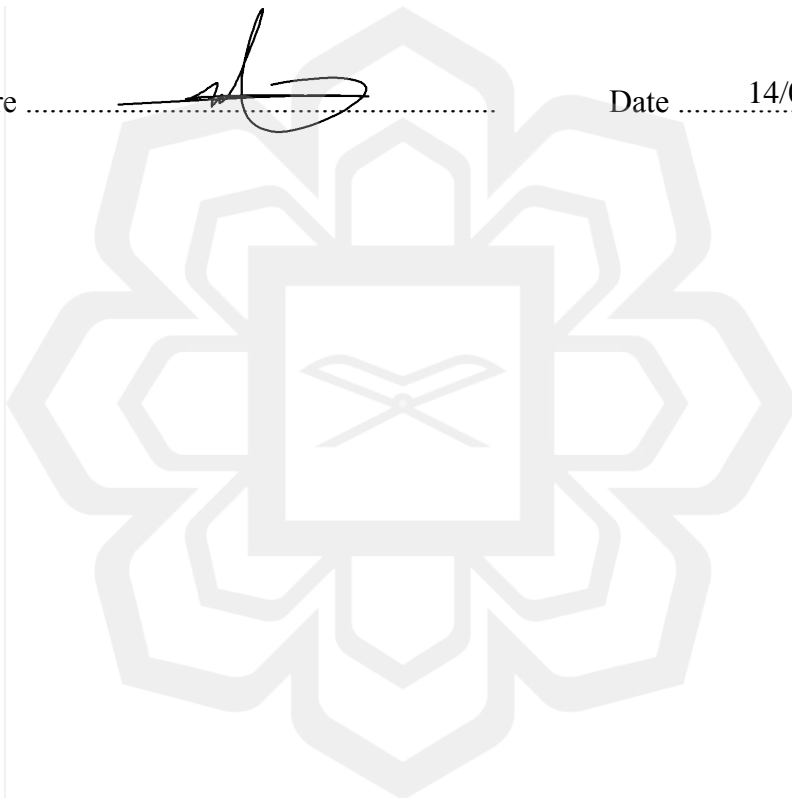
Abdelmohsen Benoudjit

Signature



Date

14/01/2022



INTERNATIONAL ISLAMIC UNIVERSITY MALAYSIA

**DECLARATION OF COPYRIGHT AND AFFIRMATION OF
FAIR USE OF UNPUBLISHED RESEARCH**

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

I declare that the copyright holders of this thesis are jointly owned by the student and IIUM.


Copyright © 2021 Abdelmohsen Benoudjit and International Islamic University Malaysia. All rights reserved.

No part of this unpublished research may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise without prior written permission of the copyright holder except as provided below.

1. Any material contained in or derived from this unpublished research may be used by others in their writing with due acknowledgement.
2. IIUM or its library will have the right to make and transmit copies (print or electronic) for institutional and academic purposes.
3. The IIUM library will have the right to make, store in a retrieved system and supply copies of this unpublished research if requested by other universities and research libraries.

By signing this form, I acknowledged that I have read and understand the IIUM Intellectual Property Right and Commercialization policy.

Affirmed by Abdelmohsen Benoudjit


.....
Signature

14/01/2022
.....
Date

ACKNOWLEDGEMENTS

Thanks to Allah for granting me patience and perseverance to accomplish this thesis successfully. Indeed, without His Help and will, nothing is accomplished.

Firstly, it is my pleasure to dedicate this work to my dear parents *Azeddine* and *Liala*, my wife *Maroua*, my daughter *Sajeda Rafif*, my son *Mohamed Nouh*, my sister *Moufida*, and my brothers *Yacine* and *Zakaria* who granted me the gift of their unwavering belief in my ability to accomplish this goal: thank you for your support and patience.

I take this opportunity to express my deep appreciation and sincere gratitude to my supervisor *Associate Professor Dr. Wan Wardatul Amani Wan Salim* and for her significant dedicated guidance and warm support at every stage of my research. Your determination in helping me was without end and it let me achieve my goals. I will never forget your help. Thank you for this opportunity.

I would also like to extend my sincere thanks to *Dr. Mohd Firdaus Bin Abd Wahab*, *Prof. Nassereldeen Ahmed Kabbashi* and all my colleagues for their assistance and suggestions in completing this thesis.

I wish to express my appreciation and thanks to those who provided their time, efforts, and support for this project. nanoSkunkWorkX team all lectures of BTE department. To the members of my dissertation committee, thank you for sticking with me.

Finally, special thanks to *Prof. Benoudjit Azeddine* for his continuous support, encouragement, and leadership, and for that, I will be forever grateful.

TABLE OF CONTENTS

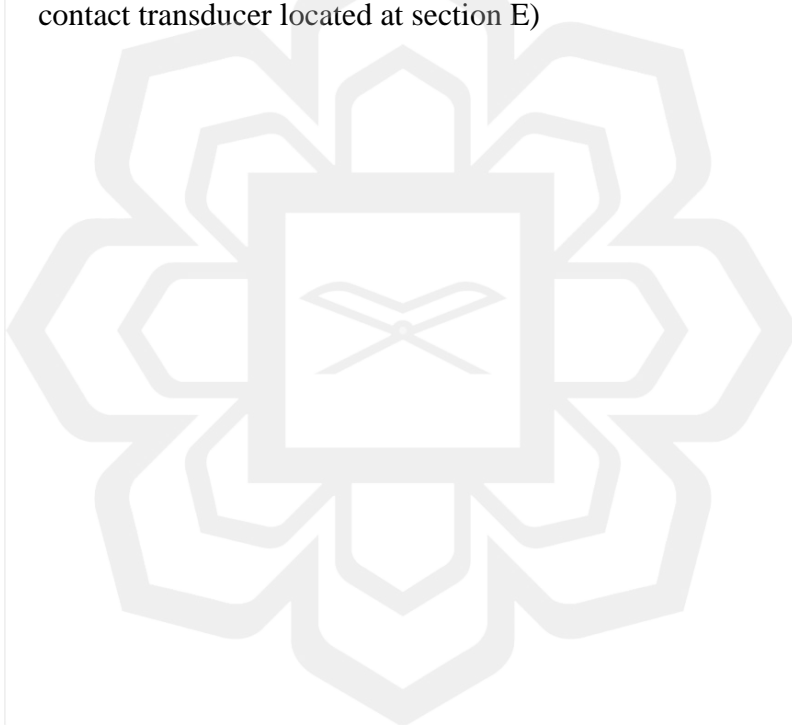
Abstract	ii
Abstract in Arabic	iii
Approval Page.....	iv
Declaration	v
Copyright Page.....	vi
Acknowledgements	vii
Table of contents	viii
List of Tables	xi
List of Figures	xii
List of Abbreviations	xvii
List of Notations	xviii
List of Symbols	xix
CHAPTER ONE	1
INTRODUCTION.....	1
1.1 Background of the study	1
1.2 Problem statement	4
1.3 Objectives	6
1.4 Research philosophy	7
1.5 Research methodology.....	7
1.6 Research scope.....	9
1.7 Chapter summary.....	9
CHAPTER TWO	11
LITERATURE REVIEW	11
2.1 Introduction.....	11
2.2 Mobile sensor technology for surface water quality monitoring.....	12
2.3 Ion-selective electrodes (ISEs)	15
2.4 All solid-state ion-selective electrodes (AS-ISEs)	16
2.5 All-solid-state ammonium ion-selective electrodes (AS-NH ₄ ⁺ ISEs)	17
2.5.1 Conductive Polymer as Solid Contact Transducer for an All-Solid-State Ammonium Ion-Selective Electrodes (AS-NH ₄ ⁺ ISEs).....	18
2.5.2 Conductive Polymer as Ionophore-Free Ion-Selective Membrane (ISM) for an All-Solid-State Ammonium Ion-Selective Electrode (AS-NH ₄ ⁺ ISEs).....	20
2.6 Characterization of all-solid-state ion-selective electrodes	26
2.6.1 Setup of Cyclic Voltammetry (CV)	26
2.6.2 Screen-Printed Electrodes (SPEs).....	26
2.6.3 Electrochemical Characterization	27
2.6.3.1 Electrochemical Reversibility.....	28
2.6.3.2 Mass Transport Properties	29
2.6.3.3 Stability.....	29
2.6.4 Sensitivity.....	30
2.6.5 Linear Range and Detection Limit.....	30

2.7 Summary	32
CHAPTER THREE	33
MATERIALS AND METHODOLOGY	33
3.1 Introduction.....	33
3.2 Apparatus and accessories	34
3.3 Chemicals and reagents	34
3.4 Preparation of electrolyte solution.....	35
3.4.1 Potassium Ferricyanide ($K_3 [Fe(CN)_6]$)	35
3.4.2 Phosphate-Buffered Saline (PBS) Solution	35
3.5 Electrode modifications.....	36
3.5.1 Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) Solid Contact Transducer Deposition	36
3.5.1.1 Pre-Treatment of Screen-Printed Electrodes (SPEs)	36
3.5.1.2 Preparation of Electropolymerization Electrodeposition Solution.....	37
3.5.1.3 Electropolymerization Deposition of PEDOT:PSS on Working Electrodes as a Solid Contact Transducer	37
3.5.2 Setup for Dynamic Measurement Conditions	39
3.5.3 Fabrication of All-Solid-State Ammonium Ion-Selective Electrodes (AS-NH ₄ ⁺ ISEs)	40
3.5.3.1 Preparation of Ammonium Ion-Selective Membrane (NH ₄ ⁺ ISM) Solution	40
3.5.3.2 Deposition of Ammonium Ion-Selective Membrane (NH ₄ ⁺ ISM)	41
3.6 Characterization of poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) soild contact transducer	42
3.6.1 Morphology of PEDOT:PSS.....	42
3.6.2 Cyclic Voltammetry (CV) of PEDOT:PSS.....	43
3.6.2.1 Electrochemical Reversibility.....	43
3.6.2.2 Mass Transport Properties	44
3.7 Stability of Poly(3,4-ethylenedioxythiophene):poly (styrene sulfonate) (PEDOT:PSS) solid contact transducer in static measurEmEnts conditions	44
3.7.1 Adhesion of PEDOT:PSS Solid Contact Transducer on Screen-Printed Electrodes (SPEs)	44
3.7.2 Repetitive CV Cycles.....	45
3.7.3 Statistical Analyses of CV Cycles	45
3.8 Electrochemical performance of PEDOT:PSS/SPCEs in dynamic measurement conditions	46
3.9 Characterization of all-solid-state ammonium ion-selective electrodes (AS-NH ₄ ⁺ ISEs).....	48
3.9.1.1 Fourier-Transform Infrared (FTIR) Spectroscopy	48
3.9.1.2 Sensitivity and Detection Limit of All-Solid-State Ammonium Ion-Selective Electrodes (AS-NH ₄ ⁺ ISEs)	48
3.10 Summary	49

CHAPTER FOUR	50
RESULTS AND DISCUSSION	50
4.1 INTRODUCTION	50
4.2 Characterization of the electropolymerized PEDOT:PSS on screen- printed carbon and platinum electrodes (SPCEs and SPPEs) as a solid contact transducer	51
4.2.1 Surface Morphology of PEDOT:PSS/SPEs.....	51
4.2.2 Cyclic Voltammetry (CV) Analysis of PEDOT:PSS/SPEs	54
4.2.2.1 Electrochemical Reversibility of PEDOT:PSS/SPEs	54
4.2.2.2 Electron Transfer Properties of PEDOT:PSS/SPCEs and PEDOT:PSS /SPPEs.....	57
4.3 Stability of electropolymerized PEDOT:PSS on screen-printed carbon and platinum electrodes (SPCEs and SPPEs) as a solid contact transducer in static measurements conditions.....	59
4.3.1 Adhesion of PEDOT:PSS to SPCEs and SPPEs.....	59
4.3.2 Measurement Drift of Repetitive CV Cycles of PEDOT:PSS/SPCEs and PEDOT:PSS/SPPEs	60
4.4 Investigating the electrochemical performance of electropolymerized PEDOT:PSS on screen-printed carbon electrodeS (SPcEs) as a solid contact transducer in dynamic measurements condition	64
4.4.1 Electrochemical Performance of PEDOT:PSS Before and After Flow Rates.....	65
4.4.2 Electrochemical Performance of PEDOT:PSS Under Different Flow Rates	67
4.4.3 Effect of The Velocity (v) on The Oxidation/Reduction Peak potential (E_p) and Peak Current (I_p).....	69
4.5 fabrication and evaluation of all-solid-state ammonium ion-selective electrodes (AS-NH ₄ ⁺ ISEs) BASED spce by two-steps process	72
4.5.1 Electropolymerization Deposition of PEDOT:PSS onto SPCEs ..	72
4.5.2 Electropolymerization Deposition of Po-PD on PEDOT:PSS/SPCEs	75
4.5.3 Fourier-Transform Infrared Spectroscopy (FTIR).....	76
4.5.4 Calibration Curve of AS-NH ₄ ⁺ ISEs	79
4.6 Summary.....	81
CHAPTER FIVE	83
CONCLUSION AND RECOMMENDATION	83
5.1 Conclusion	83
5.2 Recommendations for future work	85
REFERENCES	87
PUBLICATIONS	93
Appendix A	94
Appendix B	99
Appendix C	100

LIST OF TABLES

Table 2.1 All-solid state ammonium ion-selective electrodes (AS-NH ₄ ⁺ ISEs) based of nonactin ionophore for application in aqueous solutions.	24
Table 2.2 All-solid state ammonium ion-selective electrodes (AS-NH ₄ ⁺ ISEs) based of ionophore-free ion-selective membrane for application in aqueous solutions.	25
Table 3.1 CV setup for the activation process of the screen-printed carbon and platinum electrodes (SPCEs, SPPEs)	37
Table 4.1 Flow rate, area, and velocity of the ferricyanide solution at a different section of the dynamic measurements conditions study setup (solid contact transducer located at section E)	70



LIST OF FIGURES

- Figure 1.1 Methodology flowchart to develop a stable solid contact transducer for all-solid-state ammonium ion-selective electrodes (AS-NH₄⁺ISEs) based screen-printed carbon electrodes (SPCEs) 8
- Figure 2.1 Photograph images of a mobile sensor prototype with an integrated commercially available temperature sensor tested in aquaculture ponds and rivers. 12
- Figure 2.2 An overview of the mobile sensor platform and the sensing cell components; (a) mobile sensor components: (1) bottom part, (2) top part, (3) holder, (4) water pump, (5) microcontroller / IoT platform, and (6) sensing cell; (b) The sensing cell components: (I) chamber, (II) cup, (III) inlet, (IV) outlet, (V) sensor connector; (c) inside view of the sensing cell components: (VI) screen-printed carbon electrode (SPCE). 13
- Figure 2.3 Three main steps involved in the mobile sensor operation: 1) sampling, 2) sensing, and 3) data storage. The sampling step is taking samples from the water surface to the sensing cell using a pump. When the sample is in the sensing cell, the measurements are conducted by the sensor. After that, all the measurements are stored for further processing. 14
- Figure 2.4 Key components of all-solid-state ion-selective electrodes (AS-ISEs). The electrode of the AS ISE is usually an SPE consisting of a counter electrode (CE), a working electrode (WE), and a reference electrode (RE). The AS-ISEs key components are an ion-selective membrane (ISM), in this case for NH₄⁺, and a solid contact transducer deposited on the SPE made from carbon, platinum, or gold. 17
- Figure 2.5 Chemical structure of poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate), (PEDOT:PSS), and the conjugated single and double bonds along the polymer chain which conduct electrons. PEDOT is a conjugated polymer and carries positive charges and is based on polythiophene. PSS is made up of sodium polystyrene sulfonate, which is a sulfonated polystyrene. Part of the sulfonyl groups are deprotonated and carry a negative charge. PEDOT:PSS is p-type doping; the electron moves directly from the highest occupied molecular orbital (HOMO) of the polymer to the dopant species and creates a hole in the polymer backbone. 20
- Figure 2.6 Chemical structure of the ionophores used in an ion-selective membrane (ISM) for all-solid-state ammonium ion-selective electrodes (AS-NH₄⁺ISEs) fabrication; (a) Chemical structure of nonactin, (b)

Nonactin-complexed NH_4^+ , (c) Dibenzyl ether derivatives (DBE) (Cuartero et al., 2020). 22

Figure 2.7 A cyclic voltammogram using potassium ferricyanide, $\text{K}_3[\text{Fe}(\text{CN})_6]$ as redox-active analyte. The potential sweeps from V1 to V2 to reduce $\text{Fe}(\text{CN})_6^{3-}$ to $\text{Fe}(\text{CN})_6^{4-}$ and reverse to V2 to V1 to oxidize $\text{Fe}(\text{CN})_6^{4-}$ to $\text{Fe}(\text{CN})_6^{3-}$. The anodic and cathodic peak currents (I_{pa} , I_{pc}) and peak potentials (E_{pa} , E_{pc}) are important CV characteristics (Nurul Izzati, 2020). 28

Figure 2.8 (a) Potentiometry measurements produced by measuring the electrode's response in increasing concentration of standard solutions containing known concentration of the target analyte; (b) calibration curve. 31

Figure 3.1 Schematic of the fabrication process of PEDOT:PSS electrodes by electropolymerization deposition (EPD) of EDOT/NaPSS/ LiClO_4 solution using galvanostatic mode on screen-printed carbon electrode (SPCE) and screen-printed platinum electrode (SPPE). A screen-printed electrode (SPE) consists of a counter electrode (CE), a working electrode (WE), and a reference electrode (RE). 38

Figure 3.2 Experiment set-up to investigate the electrochemical performance of the electropolymerized deposited PEDOT:PSS solid contact transducer on screen-printed carbon electrodes (SPCEs) in dynamic measurement conditions. (1) A syringe pump was used to create a constant flow rate of solution into the flow cell. (2) 60 ml syringe was placed at the syringe pump, and the syringe was filled with 0.1 M potassium ferricyanide solution. (3) silicon tube to connect (2) and (5). (4) Holder of (5) to make sure that it is not moving. (5) A sensing cell. (6) Beaker. (7) A PEDOT:PSS/SPCEs was placed in the sensing cell to undergo the CV measurements, where the working electrode was placed horizontally. (9) Potentiostat was connected to the PEDOT:PSS/SPCE to do the measurements. 40

Figure 3.3 Fabrication process of all-solid-state ammonium ion-selective electrode (AS- NH_4^+ ISEs) Po-PD/PEDOT:PSS/SPCE by (Step one) electropolymerization deposition (EPD) of PEDOT:PSS onto the working electrode (WEs) surface using galvanostatic mode; (Step two) EPD of Po-PD onto PEDOT:PSS/SPCE using cyclic voltammetry. A screen-printed carbon electrode (SPCE) was used, which consists of a counter electrode (CE), working electrode (WE), and reference electrode (RE). 42

Figure 3.4 The different sections of the electrochemical stability study of SPCE/PEDOT:PSS in dynamic measurements condition, (a) sensing cell dimensions in millimetre (mm), (b) different setup sections. The setup was divided into sections based on the area where the flow is moving. 47

- Figure 4.1 Scanning electron microscope (SEM) images of the surface morphology of unmodified working electrodes (WEs) before EPD for (a) WE of screen-printed carbon electrode (SPCE), (b) WE of the screen-printed platinum electrode (SPPE). The unmodified surface of SPCEs showed a flaky sheet structure compared to unmodified SPPEs, which showed a porous structure. Magnification used was 1000 x, 2000 x, and accelerating voltage used was 8.0 kV. 52
- Figure 4.2 Scanning electron microscope (SEM) images of the surface morphology of the modified working electrodes (WEs) for (a) screen-printed carbon electrode SPCE, and (b) screen-printed platinum electrode SPPE. The results showed that the average area of the PEDOT:PSS/SPCEs globules was almost three times smaller compared to PEDOT:PSS/SPPEs. The average area of PEDOT:PSS/SPCEs and PEDOT:PSS/SPPEs globules was $1.63 \mu\text{m}^2$ and $4.66 \mu\text{m}^2$ respectively. Magnification 1000 x and accelerating voltage of 8.0 kV. 53
- Figure 4.3 Cyclic voltammogram (CV) and peak-to-peak potential separation (ΔE_p) in 0.1 M $\text{K}_3[\text{Fe}(\text{CN})_6]$ at a scan rate of 100 mV/s of SPCEs, SPPEs, PEDOT:PSS/SPCEs and PEDOT:PSS/SPPEs; (a) cyclic voltammogram graphs, (b) Peak-to-peak potential separation (ΔE_p), and (c) anodic peak potential (I_{pa}). Error bar: standard deviation. Number of samples, $n=3$. The results suggest that the redox system of PEDOT:PSS/SPCEs and PEDOT:PSS/SPPEs behave in either a quasi-reversible or irreversible manner owing to larger ΔE_p . 55
- Figure 4.4 Anodic peak potential (E_{pa}) against the log of scan rate ($\log V/s$) for unmodified electrodes of (a) SPCEs, (b) SPPEs, and modified electrodes of (c) PEDOT:PSS/SPCEs, and (d) PEDOT:PSS/SPPEs. The number of samples, $n=3$. The results showed a linear relation between E_{pa} versus the log of scan rate ($\log V/s$), which means the quasi-reversibility of the electron transfer was confirmed. 57
- Figure 4.5 Anodic peak currents versus root-squared scan rate plots of unmodified electrodes; (a) SPCE, (b) SPPE, and modified electrodes; (c) PEDOT:PSS/SPCE, and (d) PEDOT:PSS/SPPE. The results showed linearity for all electrodes ($R^2 = 0.9$) with different slopes. The results indicated that electropolymerized deposited PEDOT:PSS into both electrodes enhanced the electron diffusion with 2-order of magnitude and enabled the absorption of a molecule that can lead to transducer fouling. 58
- Figure 4.6 Repetitive CV cycles in a redox solution of $\text{K}_3[\text{Fe}(\text{CN})_6]$ 0.1 M for 30 days for (a) PEDOT:PSS/SPCEs, and (b) PEDOT:PSS/SPPEs. The scan rate was 100 mV/s. Oxidation and reduction peak current (I_{pa} , I_{pc}) for the modified electrodes in $\text{K}_3[\text{Fe}(\text{CN})_6]$ for (a) PEDOT:PSS/SPCEs, and (b) PEDOT:PSS/SPPEs. Scan rate was 100 mV/s with measurements made daily for 30 days. The results suggest that the electropolymerized PEDOT:PSS has good adhesion to SPCEs

and SPPEs working electrode, but the baseline signal fluctuates within 100 μ A. 60

Figure 4.7 Cycle stability profile for the initial cycle, 500, 1000, 1500, 2000, 2500, and 3000 cycles in PBS pH=7.1. Scan rate 100 mV/s, for (a) PEDOT:PSS/SPCEs, (b) PEDOT:PSS/SPPEs. Results suggest that the modified electrodes have both good repetitive CV cycles for 12 hours (no change in the CV shape); the p values are insignificant using the Bartlett test for both electrodes (0.91 and 0.98). 62

Figure 4.8 Cycle stability profile for measurements made from day 1 to day 30 for (a) PEDOT:PSS/SPCEs, and (b) PEDOT:PSS/SPPEs in PBS, pH=7.1, at a potential scan rate of 100 mV/s. The results suggest that both electrodes have promising cycle stability in liquid media for 30 days; maintaining stability over prolonged storage is considered important for mobile sensor operation. The p values are insignificant using the Bartlett test for both electrodes (0.97 and 0.96). 64

Figure 4.9 Oxidation/reduction peak potential (E_{pa} , E_{pc}) of the PEDOT:PSS/SPCE after it was exposed to four different flow rates 10, 20, 30, and 40 ml/min of 0.1 M potassium ferricyanide $K_3[Fe(CN)_6]$ solution. The results showed that the effect of the flow rates on both E_{pa} and E_{pc} was negligible, which means the PEDOT:PSS/SPCE preserved its electron transfer ability due to its well attached to the electrode surface within the flow rates that is suitable to be used with a micropump. 66

Figure 4.10 Oxidation/reduction peak current (I_{pa} , I_{pc}) of the PEDOT:PSS/SPCE after it was exposed to four different flow rates 10, 20, 30, and 40 ml/min of 0.1 M potassium ferricyanide $K_3[Fe(CN)_6]$ solution. The results showed that the effect of flow rate on both I_{pa} and I_{pc} was negligible, which means the PEDOT:PSS/SPCE preserved its integrity. The results confirmed that the PEDOT:PSS was well attached to SPCEs working electrodes (WEs) within the flow rates that is suitable to be used with a micropump. 66

Figure 4.11 Oxidation/reduction peak potential (E_{pa} , E_{pc}) of the PEDOT:PSS/SPCE after it exposed to four different flow rates of 0.1 M of potassium ferricyanide $K_3[Fe(CN)_6]$ (a) 10 ml/min, (b) 20 ml/min, (c) 30 ml/min, and (c) 40 ml/min. The results showed that the flow rate of 10, 20, 30, and 40 ml/min did not affect the E_{pa} and E_{pc} . 68

Figure 4.12 Oxidation/reduction peak current (I_{pa} , I_{pc}) of the PEDOT:PSS/SPCEs after they were exposed to four different flow rates of 0.1 M potassium ferricyanide $K_3[Fe(CN)_6]$ (a) 10 ml/min, (b) 20 ml/min, (c) 30 ml/min, and (c) 40 ml/min. the results showed that I_{pa} and I_{pc} slightly fluctuated with varying flow rates, and no specific trend was observed. 68

Figure 4.13 Oxidation/reduction peak potential (E_{pa} , E_{pc}) of the PEDOT:PSS/SPCEs versus velocity of 0.1 M potassium ferricyanide

K₃[Fe(CN)₆] liquid flow at section (E). The results showed no effect of velocity on the E_{pc} and E_{pa} of the PEDOT:PSS/SPCEs solid contact transducer. 71

Figure 4.14 Oxidation/reduction peak current (I_{pa} , I_{pc}) of the PEDOT:PSS/SPCEs versus velocity of 0.1 M potassium ferricyanide K₃[Fe(CN)₆] liquid flow at section (E). The results showed no effect of velocity on the I_{pc} and I_{pa} of the PEDOT:PSS/SPCEs solid contact transducer. 71

Figure 4.15 Scanning electron microscope (SEM) image of screen-printed carbon electrode (SPCE) and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), magnification 1000x and accelerating voltages of 8.0 kV, (a) SEM image of the SPCE, (b) SEM image of the PEDOT:PSS/SPCE. 73

Figure 4.16 (a) Cyclic voltammetry (CV) graphs in potassium ferricyanide (K₃[Fe(CN)₆]) for unmodified screen-printed carbon electrode (SPCE) and SPCEs' electropolymerized with poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) (PEDOT:PSS/SPCEs); scan rate of 100 mV/s, and (b) SPCE and PEDOT:PSS/SPCE linear regression of the anodic/cathodic peak current (I_{pa} , I_{pc}) vs. the square root of the scan rate ($mV^{1/2}$). 74

Figure 4.17 Cyclic voltammograms obtained during electropolymerization of 0.08 mM o-PD at the potential range of 0 to 0.8 V and scan rate of 50 mV/s. The results show the peak current decreased significantly with increasing cycle, which means that the electrode surface is covered with an insulative layer of ISM. 76

Figure 4.18 FTIR spectra of modified SPCE, spectrum range between 600 and 4000 cm⁻¹ (a) screen-printed carbon electrode (SPCE) (b) PEDOT:PSS/SPCE, (c) Po-PD/SPCE, and (d) Po-PD/PEDOT:PSS/SPCE. Results suggested that the electropolymerization deposition of PEDOT:PSS onto SPCE and Po-PD onto PEDOT:PSS/SPCE were conducted successfully. 78

Figure 4.19 All-solid-state ammonium ion-selective electrodes (AS-NH₄⁺ISEs) calibration showing the (a) chronopotentiometry measurements, and (b) the calibration curve. Po-PD/PEDOT:PSS/SPCEs reached a detection limit of 5.7×10^{-5} M and has a linear range of 10^{-3} to 1^{-1} M. A higher slope means a more sensitive sensor; PEDOT:PSS/SPCEs showed the highest slope in this study compared to Po-PD/PEDOT:PSS/SPCEs. 80

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 ₂ SO ₄	Sulfuric acid
HCl	Hydrochloric acid
K ₃ [Fe(CN) ₆]	Potassium ferricyanide
KCl	Potassium chloride
KH ₂ PO ₄	Monopotassium phosphate and
LiClO ₄	Lithium perchlorate
Na ₂ HPO 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-NH₄⁺ISEs can be

ionophore-based or ionophore-free (Cuartero et al., 2020). Recent research showed that AS-NH₄⁺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 NH₄⁺ 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-NH₄⁺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 (O₂ and CO₂) 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-NH₄⁺ISEs. Therefore, this work aims to develop a stable AS-NH₄⁺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-NH₄⁺ISEs) are the solid contact transducer and the ion-selective membrane (ISM). The stable performance of the AS-NH₄⁺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-NH₄⁺ISEs. Therefore, this work aims to develop stable AS-NH₄⁺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 NH₄⁺ ions play a critical role in the occurrence and