pH sensors with high sensitivity utilising coulometric transduction method –

comparison of solid-contact ion-selective electrode and polyaniline-based ion-selective electrode

Åbo Akademi University

Faculty of Science and Engineering

HIU MUN MAN

Master's programme in Excellence in Analytical Chemistry

Degree project in Analytical chemistry, 30 ECTS

Supervisor: Tingting Han (Åbo Akademi University)

Co-supervisors: Prof. Johan Bobacka (Åbo Akademi University)

Prof. Ivo Leito (University of Tartu)

August 2019

ABSTRACT

This thesis compares the analytical performance of solid-contact ion-selective electrodes (SC-ISEs) and polyaniline-based ion-selective electrodes for the determination of pH using a newly developed coulometric signal transduction readout method. For the SC-ISEs, the conducting polymer poly(styrene-sulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT(PSS)) served as an ion-to-electron transducer. The coulometric transduction readout method was able to amplify the analytical signal by increasing the thickness of the solid-contact layer. It also was shown that the thinner the ion-selective membrane, the shorter the response time, which could be associated with a more rapid ion transport between the ion-selective membrane and the solid-contact layer.

For the polyaniline-based ISEs, the coulometric response was found to be not entirely proportional to pH. This could be explained by the cyclic voltammogram of polyaniline which contains several peaks, meaning that the redox capacitance of polyaniline depends on the potential, as does the coulometric response. Since the conducting polymer worked both as an ion-to-electron transducer and as a sensing membrane, the chronoamperometric response of the polyaniline-based pH sensor was directly affected by interfering ions. By integrating the resulting current against time, the coulometric signal readout has shown to be useful in reducing the noise level. Under optimised conditions, a 10 mC PEDOT(PSS) solid-contact pH sensor covered with a drop-casted ion-selective membrane was able to detect 0.18 % change in concentration; a 50-cycle polyaniline-based pH sensor could detect a 0.36% change in concentration using the novel coulometric transduction method.

Keywords: coulometric transduction, solid-contact ion-selective electrode, pH sensor, high sensitivity, polyaniline

PREFACE

This master's thesis was conducted at the Laboratory of Analytical Chemistry, Åbo Akademi University, within the Erasmus Mundus joint master's programme "Excellence in Analytical Chemistry" (EACH).

I must thank my supervisors in Åbo Akademi University, Professor Johan Bobacka and Tingting Han for their patience and guidance throughout the project.

I would like to express my gratitude to Professor Ivo Leito for his valuable support in the thesis. Huge thanks to him and Dr. Anu Teearu-Ojakäär for the coordination of the programme EACH as I am extremely grateful to be a part of this programme.

Special thanks to my dearest friends and colleagues in Tartu and Turku, without whom I would not have been able to stay motivated in difficult times.

Finally, my sincerest and deepest thanks to my friends and family scattered across the globe. To my old friends, my parents and my sister, thank you for your encouraging words and immense support in whatever path I pursue.

Turku, May 2019

Hiu Mun Man

CONTENTS

LIST OF SYMBOLS

a_{H+}	Activity of hydrogen ions
a_i	Activity of species i
E	Potential
E^o	Standard potential
F	Faraday's constant (96584 C mol^{-1})
f	Frequency
I	Current
Q	Charge
R	Universal gas constant (8.314 J mol^{-1} K^{-1})
T	Temperature in Kelvins
z_i	Charge of species i
Z'	Real impedance
Z''	Imaginary impedance

LIST OF ABBREVIATIONS

Ag	Silver
AgCl	Silver Chloride
CE	Counter electrode
CP	Conducting polymer
CV	Cyclic voltammetry
DOS	Bis(2-ethylhexyl) sebacate
EB	Emeraldine base
EIS	Electrochemical impedance spectroscopy
ES	Emeraldine salt
GC	Glassy carbon
ISE	Ion-selective electrode
ISM	Ion-selective membrane
KTFPB	Potassium tetrakis[3,5-bis-(trifluoromethyl)phenyl]-borate
KTpClPB	Potassium tetrakis(4-chlorophenyl)borate
LEB	Leucoemeraldine
LiAc	Lithium acetate
OCP	Open circuit potential
o-NPOE	2-nitrophenyl octyl ether
PANI	Polyaniline
PANI(Cl)	Chloride-doped polyaniline
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEDOT(PSS)	Poly(styrene-sulfonate)-doped Poly(3,4-ethylenedioxythiophene)
PNB	Pernigraniline
PSS	Poly(styrene-sulfonate)
PVC	Poly(vinyl chloride)
RE	Reference electrode
SC-ISE	Solid contact-ion selective electrode
THF	Tetrahydrofuran
WE	Working electrode

1 INTRODUCTION

Potentiometric ion sensors, or ion-selective electrodes (ISEs) are one of the most important and widely used classes of electrochemical sensors due to their desirable characteristics such as simple instrumentation, low-energy consumption, low cost, ease of use and good possibilities of miniaturisation [1-3]. An ever-growing demand in clinical, forensic and environmental analyses calls for the development of in-situ, portable and selective sensors with high sensitivity [4-6].

The development of solid-state ion-selective electrodes has removed the inconvenience brought by internal filling solution, and thus making maintenance and miniaturisation more facile [3]. However, a major problem with the initial solid-state electrodes (called coated-wire electrodes) [7] lies in the fact that the ion-to-electron transduction between the electronic substrate and the ion-selective membrane is interrupted, leading to an instability in electrode potential. A considerable amount of literature has been published on conducting polymer-based ion-selective electrodes [1-3, 8-15]. Electrically conducting polymers act as the ion-to-electron transduction mediator in ISEs owing to their electronic and ionic properties. It has been shown by Bobacka [7] that poly(3,4-ethylenedioxythiophene) (PEDOT) is a promising conducting polymer to maintain potential stability of solid-contact ion-selective electrodes due to its high redox capacitance.

In addition, since the analytical response of ISE is dependent on the logarithmic activity of the target ion, the sensitivity of the sensor is limited. A novel signal readout method based on coulometric transduction for solid-contact ion-selective electrodes was introduced by Hupa *et al.* [1] to address this issue. This method is based on the measured current that passes through the working electrode and the counter electrode, as a constant potential is held between the working electrode and the reference electrode [1-2]. As the potential of the working solid-contact ISE is held constant by a potentiostat, the change in potential at the ion selective membrane | sample boundary is compensated by an equivalent but opposing potential change in the solid-contact layer. Changes in primary ion activity in the cell produce a transient current, leading to redox reactions occurring at the conducting polymer solid contact until the potential change is fully compensated. The total cumulated charge can be obtained by integrating this measured current, which is linearly proportional to the change in potential; thus, the total charge is proportional to the change in primary ion activity. Amplification of the analytical response has been shown to be possible by manipulating the capacitance of the solid-contact

membrane [1]. The practical applications of this method were first limited by a slow response time, owing to ion-selective membrane's high resistance [1-2]. Different approaches have been successfully applied to reduce the resistance of the ion-selective membrane by increasing the area of the electrode and/or applying a thin-layer ion-selective membrane [8-10].

The main objective of this work was to compare the analytical performance between PEDOT(PSS) solid-contact ion-selective electrodes and polyaniline-based ion-selective electrodes employing the novel coulometric transduction method for the determination of pH.

This thesis is composed of five sections, including this introductory section. Section two outlines the theoretical background of techniques and materials relevant to the work. The third and fourth sections are concerned with the methodologies and the results of the research; these two sections are subdivided into two parts, separating the solid-contact pH-selective electrodes and the polyaniline-based pH sensors. The last section ties up the thesis with a brief summary as well as highlighting the need for future research.

The results in this thesis showed that the fabricated pH sensors can detect $0.18 - 0.36$ % changes in the H^+ activity, corresponding to $\Delta pH = 0.001 - 0.002$. This indicates the future possibilities of this method for the detection of extremely small changes in pH with such types of electrodes, with merits such as low cost, ease of miniaturisation and ease of fabrication.

2 BACKGROUND

2.1 Potentiometric ion sensors

2.1.1 General

A chemical sensor is defined as a device that converts chemical information into an analytically useful signal [1]. Sensing consists of two steps; molecular recognition (by recognition/ receptor element) and signal transduction (by transducer element). According to the mode of transduction, chemical sensors can be classified into optical, electrochemical, thermometric and mass-sensitive devices. Electrochemical sensors, in particular, are devices that transduce chemical information into electrical signal. They can be further distinguished into different groups according to the signal's nature: voltammetric, potentiometric, chemically-sensitive field-effect transistor and potentiometric solid electrolyte gas sensors [16].

A large and growing body of research has been focused on investigating the feasibility of disposable, wearable or wireless ISEs for the determination of essential ions such as Na^+ and K^+ in different sample matrices, e.g. soil and sweat [8-9], demonstrating the vast and far-reaching applications ISEs could offer. One of the most impactful applications of ISEs is in the clinical fields, where ISEs have become standard method of analysis in determining important parameters such as H^+, Na^+, K^+, CO_2, Ca^{2+}, Cl^- and urea in bodily fluids [17].

A typical potentiometric cell has two electrodes, a working electrode (WE) and a reference electrode (RE) immersed in a bulk solution. The reference electrode's potential is constant; and the potential of the working electrode is then measured against the reference electrode under zero-current conditions. The sensing layer, composed of a thin film or an ion selective membrane [18], is able to transform the activity of an analyte into a meaningful electrical response that is dependent upon the logarithm of the ionic activity of an analyte (a_i) according to the Nernst equation,

$$E = E^o + \frac{2.303\ RT}{z_i F} \log a_i, \qquad \textit{(Eq. 1)}$$

where E is the cell potential, E^o is the standard cell potential, R is the real gas constant (8.314 J K^{-1} mol^{-1}), T refers to temperature in Kelvins, z_i is the ion charge transferred, and F is the Faraday's constant (96485 C mol^{-1}). For the determination of H^+ ions where $z = 1$, the Nernstian response of a functioning sensor with the ideal sensitivity will have a slope of 59.16 mV / log a_i at 25 °C. However, a sensor with the ideal sensitivity does not necessarily have the ideal

selectivity since a Nernstian response may also be observed when an interfering species exists as the only potential-determining species of ions [18].

2.1.2 Development of solid-state ion selective electrodes

A conventional ISE is comprised of a poly(vinyl chloride) (PVC) based ion selective membrane affixed to the end of a tube wherein an internal reference electrode is immersed in the internal filling solution containing the species of interest (**Figure 1a**). The internal filling solution serves as a charge exchanger between the internal reference electrode and the ion selective membrane. This ISE is then immersed in the analyte solution along with an external reference electrode. Problems arise when using a conventional ISE as the internal filling solution must be constantly maintained to ensure the potential stability of the sensor. The solution has to be in contact with the inner membrane and miniaturisation is made very difficult because of the existence of the inner filling solution.

Coated-wire electrode (CWE) proposed by Cattrall and Freiser in 1971 marks the beginning of solid-state ISEs, eliminating the need for internal filling solution in traditional ISEs (structure shown in **Figure 1b**) [19]. The development of CWE made potentiometric ion sensors with higher durability and easier construction possible [20]. However, the main issues with CWEs were related to irreproducibility and electrode potential instability due to the high charge transfer resistance between the ion-selective membrane and the electronic substrate [21]. To improve the stability of the electrode potential, solid-state ISEs have been constructed using electroactive substance that exhibits both electrical and ionic conductivities [21]. Much research attention has been devoted to electroactive conducting polymers as they function as the ion-to-electron signal transducer between the electrical conductor and ion-selective
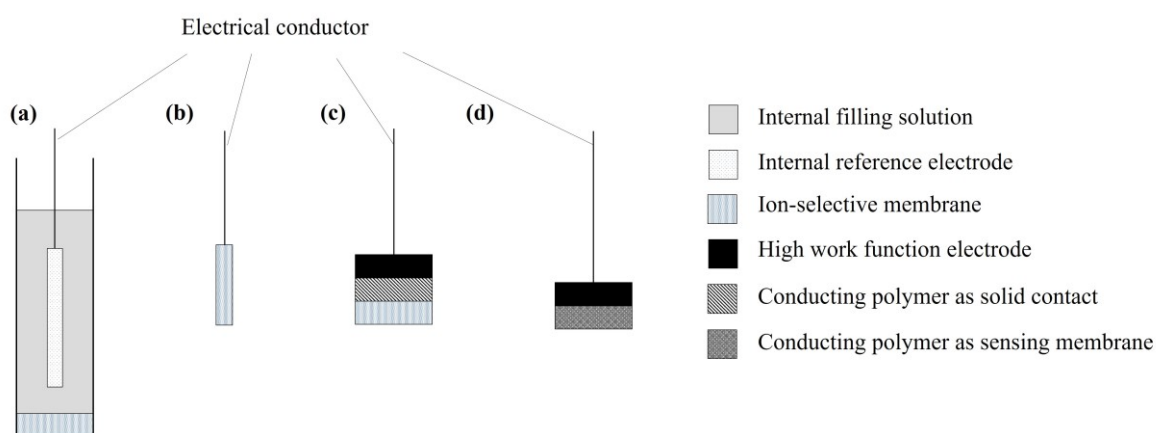
Figure 1. *Structures of ion-selective electrodes (ISEs). (a) ISE with internal filling solution and internal reference electrode, (b) coated-wire electrode, (c) ISE with conducting polymer as the solid contact, and (d) ISE with conducting polymer as the ion-sensing membrane [Adapted from reference 20].*

4

membrane (structure as illustrated in **Figure 1c**); a wide range of materials including hydrogel with Ag/AgCl, nanocarbon composites and silver composites has also been proposed to be the basis of the solid contacts of ISEs [3, 20-23].

2.1.3 Ion-selective membrane

Ion-selective membrane (ISM) is crucial in ISE as it is the recognition element of the sensor. An ISM incorporates an ionophore within a plasticised polymer matrix, most commonly PVC. ISMs typically have rather high electrical resistance; however, they should conduct charge to perform properly according to Ohm's Law. The ionophore is the charge carrier that selectively binds to the ion of interest [24].

A typical ISM is composed of around 65.5% w/w plasticiser, 33% w/w PVC, 1% w/w ionophore and 0.5% lipophilic salts dissolved in a volatile organic solvent, for example, cyclohexanone or tetrahydrofuran [24]. PVC holds all the membrane components together as well as increases the dielectric constant, resulting in a relatively higher ionic concentrations in the membrane [25]. Plasticisers such as bis(2-ethylhexyl) sebacate (DOS) and 2-nitrophenyloctyl ether (o-NPOE) are added to lower the PVC glass transition temperature, increasing the homogeneity, flexibility as well as mechanical stability of the membrane [26]. The plasticiser to PVC ratio should ideally be 2 to 1 to decrease membrane resistivity while maintaining a robust membrane structure [27]. Lipophilic salts such as potassium tetrakis[3,5-bis-(trifluoromethyl)phenyl]-borate (KTFPB) and potassium tetrakis(4-chlorophenyl)borate (KTpClPB) are ionic additives that serve to preserve the neutrality of the membrane in case of a neutral ionophore.

2.2 Conducting polymers

The era of conducting polymers (CPs) began with the discovery of electrically conducting polyacetylene films in 1970s [28]. CPs are long organic chains with a conjugated backbone (alternating single and double bonds). The continuous overlap of p_z-orbitals in the double-bond chain causes π-electrons to delocalise. Oxidation/reduction of the conjugated polymer backbone results in an excitation that generates charger carriers such as polarons, bipolarons and solitons, contributing to the significant increase in electrical conductivity in CPs [29-30].

2.2.1 Conducting polymers as solid contacts

The advance in CPs has also led to significant developments in solid-state ion selective electrodes based on conducting polymers [22]. Cadogan *et al.* first incorporated a polypyrrole

5

(PPy) based all-solid-state K$^+$-selective electrode in 1992, where PPy was used as an ion-to-electron transducer between the ion-selective membrane and the electrode [31]. The main functionalities of CPs in solid-state ISEs are outlined as follows: (1) CPs can create an ohmic contact to high work-function substances such as platinum and carbon, (2) CPs can be deposited directly onto the surface of the conductor by electrodeposition of different monomers, (3) some can be deposited from the solution due to their solubility, (4) since CPs have mixed ionic and electrical conductivity, an ionic signal can be transduced into an electronic response in the solid state [20]. The use of CPs such as PPy, poly(3-octylthiophene), poly(3,4-ethylenedioxythiophene) (PEDOT), and polyaniline (PANI) as ion-to-electron transducers has been investigated, and such polymers have shown numerous desirable characteristics; namely, good stability, cost-effectiveness, and ease of miniaturisation [1-2, 20].

2.2.2 Conducting polymers as ion sensing membrane

Conducting polymers are also incorporated into solid-state ISEs as the sensing membranes for the detection of various ions, for example, K$^+$, Ag$^+$, Ca^{2+}, Zn^{2+} and pH [20]. Some typical conducting polymers used for such applications include the derivatives of polypyrrole, polyaniline, polyindole and polycarbazole. [20]. For pH sensing, Masalles *et al.* has reported the use of electrochemically synthesised PPy doped with cobalt bis(dicarbollide), which resulted in a subpar performance when compared to the traditional glass pH sensor [32]. Other approaches towards solid-state pH sensing involve the use of PPy doped with bicarbonate on platinum electrode, polyaniline doped with Cl$^-$ on glassy carbon and on carbon fibre [33-35]. It has been shown by Lindfors and Ivaska that the dopant and the substituent of polyaniline during the electrochemical synthesis will affect the sensitivity of polyaniline membrane. Amongst polyaniline and its alkyl and N-substituted derivatives, PANI(Cl) have shown to give the best pH sensitivity [34-35].
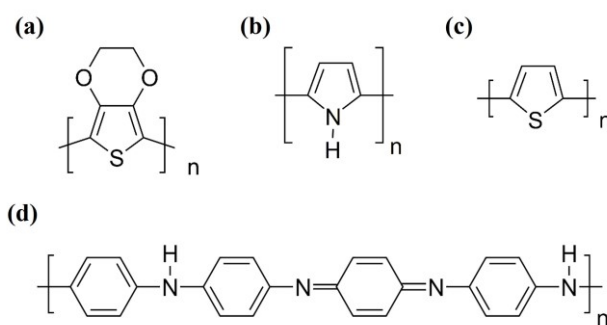

Figure 2. *Conducting polymers commonly used in ion-selective electrodes, including (a) poly(3,4-ethylenedioxythiophene), (b) polypyrrole, (c) polythiophene, and (d) polyaniline.*

2.2.3 Polyaniline

Polyaniline (PANI) is one of the most researched conducting polymers since the "rediscovery" of its high electroconductivity in the late 20th century [36-38], that has numerous attractive qualities in comparison with other conducting polymers, including facile electrosynthesis, low cost of monomer and high stability [38-39]. Polyaniline possesses several oxidation states which are all dependent on potential and pH [34]. **Figure 3** shows the schematics of three forms of polyaniline reduction/oxidation transitions, including leucoemeraldine base (LEB), emeraldine salt (ES) and pernigraniline base (PNB), which are essentially the completely-reduced, the half-oxidised and the completely-oxidised forms of polyaniline, respectively [34-36]. The only form with good electronic conductivity is ES, which arises from protonating nitrogen at the amine and imine sites in emeraldine base (EB) [41]. A strong acidic environment is therefore required to obtain ES.

PANI has found many useful applications in portable batteries, anti-corrosion agent and ion sensors [42-43]. Due to the unique chemistry of PANI, it has been incorporated in ion sensors in different ways: (a) PANI as the solid contact [44], (b) PANI-based as a single-piece electrode [45-47] , and (c) PANI as the sole component of the ion-sensing membrane [48-50] and co-workers has reported the suppression of pH sensitivity for PANI membranes that contain tridodecylmethylammonium chloride or potassium tetrakis(4-chlorophenyl)borate, indicating that certain additives in the polyaniline membrane could influence the sensitivity of PANI [38].
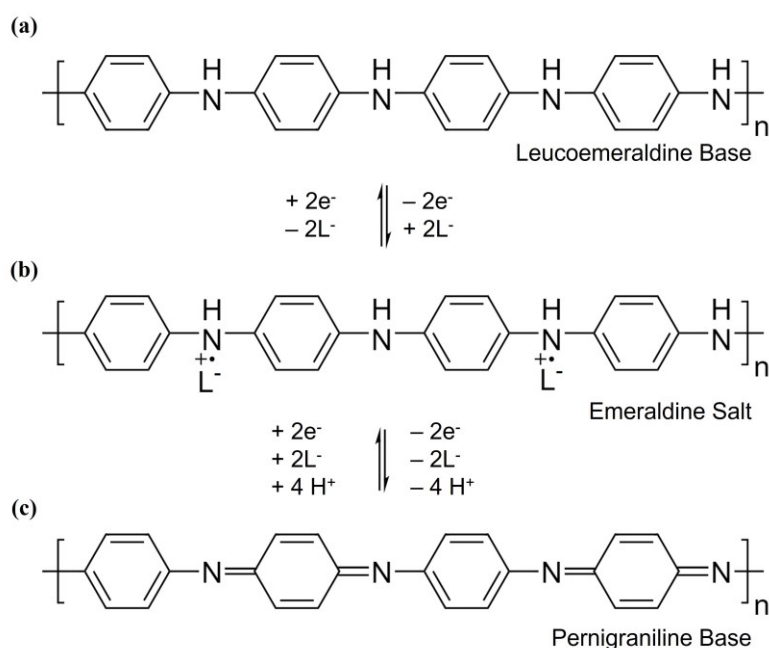
Figure 3. The redox transitions of polyaniline: (a) leucoemeraldine base (LEB), (b) emeraldine salt (ES) and (c) pernigraniline base (PNB) forms of polyaniline [Adapted from reference 34].

2.2.4 PEDOT

Poly(3,4-ethylenedioxythiophene), often abbreviated as PEDOT, is an intrinsically conductive polymer that has been fully commercialised since its discovery in the 1990s. Due to its high stability, conductivity and transparency, it has found applications in solid electrolyte capacitors, photographic films as an antistatic agent, packaging materials and touch screens [51].

PEDOT can be synthesised by polymerising 3,4-ethylenedioxythiophene (EDOT). As EDOT gets oxidised, two electrons are lost in each monomer when they couple together to form a polymer. Simultaneously, the formed polymer is oxidised forming a positively-charged conjugated PEDOT chain. It has been demonstrated that the addition of sulfonic acids is apt for balancing the positive charges, thus stabilising the polymer-counterion complex [52].

A stable dispersible complex can be obtained by polymerising EDOT with persulfate in poly(styrene sulfonic acid) solution. The PEDOT(PSS) gel complex in water dispersion can be stable for months to years depending on its concentration and variety. Different deposition methods can be applied to such complex, for example, spin-coating, doctor blading, screen printing and dip-coating [53]. In case of ion-selective electrodes, PEDOT(PSS) complex can be used as the solid contact layer, serving as the electroactive cation-exchanger. The large redox capacitance of PEDOT and its small diffusion resistance has been reported to have an electrode potential stabilising effect as it serves as a buffer against external noise when used as solid contract in ISEs [4].

PEDOT has been shown to be preferred over polypyrrole for the construction of solid-contact ion selective electrodes, because it is not as sensitive towards O_2 and pH [54]. There are, however, a few challenges associated with using electroactive polymers as solid contact of an ISE. These include their sensitivities towards oxygen, carbon dioxide and light. The movement of oxygen and carbon dioxide from solution to the solid-contact surface via the ion-selective membrane could easily affect the pH of the solution or the charge of the solid-contact [54]. Light sensitivity is another problem in SC-ISEs [55-56]. Lindfors investigated the sensitivity of light of different solid-contact electrodes; he showed that Cl doped polypyrrole and FeCN doped polypyrrole are less sensitive towards light than polystyrene sulfonate doped PEDOT and tetrafluoroborate doped poly(3-octylthiophene) [56].

2.3 Characterisation techniques

2.3.1 Constant-potential coulometry

A new coulometric transduction technique has been introduced for solid-contact ISEs based on the hypothesis that the ion sensor goes from a zero-current equilibrium state to new equilibrium state, and that there exists a considerable transient current that passes through the ion sensor [1-2]. As shown in **Figure 4**, it is conducted in a conventional three-electrode cell, consisting of a working electrode (SC-ISE), a reference electrode (RE), and a counter electrode (CE), where a constant potential between the SC-ISE and the RE is maintained by a potentiostat. A change in primary ion
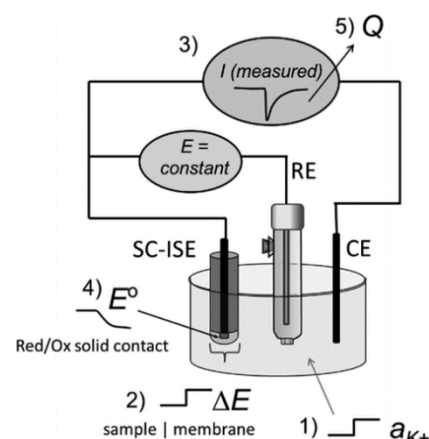
Figure 4. A schematic diagram of the new coulometric transduction technique [3].

activity in the electrochemical cell leads to a change in the potential at the solution | ion-selective membrane interface. As the potential of SC-ISE vs. RE is kept constant by a potentiostat, this boundary potential change is counterbalanced by an equivalent but opposing change in the potential of the solid- contact film, generating a transient oxidising/reducing current that passes through the sensor. This current is then measured and integrated into the total cumulated charge (Q), which is linearly related to the logarithm of primary ion activity.

Vanamo *et al.* have also shown that the analytical response can be amplified by increasing the capacitance, i.e. the thickness of the solid-contact film of the SC-ISE [2]. The use of conducting polymers as solid-contact film allows the control of the solid contact potential by altering the ionic composition and redox equilibrium of the solid-contact film, which in turn contributes to the overall electrode potential [57-58].

2.3.2 Chronoamperometry

Chronoamperometry is a pulsed technique in which the voltage of the working electrode is stepped. The subsequent current produced from the step is then recorded as a function of time. This technique gives information about diffusion processes, adsorption behaviours, rates of chemical reactions, and rates of electrode processes [59]. Regarding SC-ISEs, chronoamperometry can be used to investigate the charge transport of the conducting polymer solid-contact film [60]. Measurements are done in a three-electrode cell, consisting of a working electrode, a reference electrode and a counter electrode. The potential of the working electrode against the reference electrode is maintained by a potentiostat and current flows between the counter electrode and the working electrode.

2.3.3 Potentiometry

In potentiometry, the potential between the working electrode and the reference electrode is recorded using a voltmeter with high input impedance. With a high impedance voltmeter, it is assumed that the current flow is so small that it does not affect the measured potential. Potentiometric calibrations of the SC-ISEs are performed to ensure that the electrodes are functional, i.e. giving a Nernstian response where the response of potential against activity has a slope > 55 mV/decade.

2.3.4 Synthesis of conducting polymers

In general, the synthesis of conducting polymers can be done chemically, photochemically and electrochemically [61]. Electrochemical polymerisation can be classified into (a) galvanostatic, (b) potentiostatic and (c) potentiodynamic techniques [56]. Galvanostatic deposition involves the application of a constant current with a constant current density. The thickness of the CP films is obtained by controlling the duration of the polymerisation process. In potentiostatic polymerisation, a constant positive potential is applied for oxidative polymerisation. Both galvanostatic and potentiostatic techniques result in the conducting form of the polymer. Potentiodynamic polymerisation involves cyclic voltammetry, where a cyclic change of potential leads to a cyclic change of the CP between the conductive and non-conductive forms [61]. Electrochemical synthesis is usually carried out in a conventional three-electrode cell. The working electrode serves as the anode, where the polymerisation and deposition of the CP take place. The reference electrode controls the potential whereas the counter electrode reduces the solvent.

2.3.5 Electrochemical impedance spectroscopy (EIS)

EIS allows for the investigation of processes with different time constants using an AC signal (potential or current) within a broad frequency range (10^{-5} – 10^{7} Hz). Information about electrochemical processes such as electron transfer resistance, double-layer capacitance and specific adsorption processes can be obtained. The advantages compared to other electrochemical methods include: (1) the experimental possibility for highly-sensitive analyses since the signal may indefinitely be stable, and thus the response could be averaged over a long period of time; (2) the ability to process the signal by linearised current-voltage properties; (3) measurements are performed over a wide range of frequency; (4) the system under study is at equilibrium, meaning one does not need detailed knowledge about the electrochemical behaviour over a large range of overpotential [62].

EIS has been used to investigate the kinetics of charge transfer reactions at the solution | ISM interface, as well as the charge transfer, the capacitance and ionic diffusions of conducting polymers [63-66]. It has been shown that increasing the thickness of the solid contact film will increase the low-frequency capacitance [7].

3 EXPERIMENTAL

3.1 Part I – solid-contact pH-selective electrodes

3.1.1 Reagents and solutions

Hydrogen ionophore II (4-Nonadecylpyridine), potassium tetrakis(4-chlorophenyl) borate (KTpClPB), 2-nitrophenyl octyl ether (o-NPOE), bis(2-ethylhexyl) sebacate (DOS), poly(vinyl chloride) (PVC) and tetrahydrofuran (THF) were obtained from Fluka Analytical, and were of Selectophore purity grade. Sodium chloride (NaCl) ($\geq$99%), poly(sodium 4-styrenesulfonate (NaPSS, molecular weight ~70 000), 3,4-ethylenedioxythiophene (EDOT, 97%), hydrogen chloride (HCl, ~37%) were purchased from Sigma Aldrich. Deionised water (ELGA Purelab Ultra, U.K.) was used for all measurements.

3.1.2 Preparation of electrodes

Glassy carbon (GC) working electrodes (diameter = 3mm) encased in PVC housing were polished with sandpapers (of grit sizes 600, 1200, 2400 µm), diamond paste (15, 9, 1 µm) and 0.3 µm Al_2O_3 paste. The polished electrodes were ultrasonicated in ethanol and then in deionised water for 5 minutes, respectively.

Polymerisation solution (0.01 M EDOT + 0.1 M NaPSS) was stirred overnight for a complete monomer dissolution. In a conventional three-electrode electrochemical cell, consisting of a double junction Ag/AgCl/ 3 M KCl/ 1 M LiAc reference electrode (Metrohm, the Netherlands), a glassy carbon working electrode and a glassy carbon rod as auxiliary electrode, the polymerisation solution was purged with nitrogen gas ($\geq$ 99%) for 15 min prior to the polymerisation, after which the nitrogen tubing was lifted above the solution, creating a gas blanket. The deposition of solid contacts PEDOT(PSS) on the surface of the working GC was performed galvanostatically with an Autolab General Purpose Electrochemical System (PGSTAT20, FRA2, AUTOLAB, Eco Chemie, B.V., The Netherlands). A constant current of 0.014 mA/cm^2 was applied for 71.4, 357, 714, 1071 and 1428 s to obtain polymerisation charges of 1, 5, 10, 15 and 20 mC, respectively. The GC/PEDOT electrodes were air-dried overnight before further modifications with ion selective membrane (ISM).

Solid-contact ion-selective electrodes (SC-ISE) with thin-layer ISM were fabricated by spin-coating the H$^+$-selective membrane cocktail onto the working GC electrodes (of polymerisation charges 1, 5 and 10 mC) placed on the rotator. One to three 15 µL drops of the membrane cocktail were dispensed onto the surface of the electrode with a rotation speed of 1500 rpm.

Thick layered SC-ISEs were prepared by drop casting 50 µL of the H^+-selective membrane cocktail onto the working electrodes (of polymerisation charges 1, 5, 10, 15, 20 mC), covering both the GC surface and the PVC housing. The modified fabricated electrodes were air-dried overnight and then conditioned in 0.01 M HCl overnight. All electrodes were stored in 0.01 M HCl solution in-between experiments. The composition of the H^+-selective membrane (dry mass = 15%) was 1 wt% hydrogen selective ionophore II, 1 wt% KTpClPB, 68% wt% o-NPOE, and 30 wt% PVC dissolved in THF. The molar ratio of ionophore to KTpClPB was 1.8:1.

3.1.3 Potentiometry and chronoamperometry

Potentiometric measurements were carried out using a multichannel potentiometer (EMF16 Interface, Lawson Laboratories, Inc.) over a concentration range from 10^{-2} to $10^{-5.6}$ M HCl, with working SC-ISEs and a reference electrode (a double junction Ag/AgCl/ 3 M KCl/ 1 M LiAc reference electrode). A plot of open circuit potential was then plotted against the logarithm of activity to confirm the proper functioning of H^+-selective SC-ISEs (> 55 mV/decade corresponding to the theoretical slope). Chronoamperometric measurements were performed with Iviumstat (Ivium Technologies, The Netherlands) in a three-electrode cell containing a working SC-ISE, a counter GC rod and a reference electrode, over the concentration range of 10^{-2} to $10^{-5.6}$ M.

For both potentiometric and chronoamperometric measurements, the starting solution was 100 mL of either 0.01 M HCl or 0.01 M HCl + 0.1 M NaCl, gradually diluted with deionised water or 0.1 M NaCl, respectively. The dilutions were carried out by two Metrohm 700 Dosino units connected to and controlled by a Metrohm 711 Liquino system (Metrohm, the Netherlands). Dilutions were performed in 20 steps with a 5-min pause between each dilution allowing for equilibration. The dilution system removes 32.4 mL of the electrolyte and replaces it with an equal amount of deionised water or 0.1 M NaCl for each dilution, resulting in $\Delta \log a_H^+ = 0.18$ decades per dilution step. Manual dilutions were also performed for potentiometric measurements, over the concentration ranges $10^{-2} – 10^{-5}$ M HCl, gradually diluted with deionised water.

Sensitivity tests were performed potentiometrically and chronoamperometrically. In an electrochemical cell consisting of a double-junction reference electrode, a working SC-ISE (and a counter GC rod for chronoamperometric measurements) immersed in 50 mL of 5 mM HCl + 0.1 M NaCl, varying volumes (5 – 50 µL) of 0.1 M HCl + 0.1 M NaCl solution was added under constant stirring.

3.1.4 *Electrochemical impedance spectroscopy*

Electrochemical impedance spectroscopy was carried out using an Autolab General Purpose Electrochemical System and Autolab Frequency Response Analyzer System (PGSTAT20, FRA2, AUTOLAB, Eco Chemie, B.V., The Netherlands). A three-electrode cell containing the working GC electrode, a counter GC rod and a reference electrode (double junction Ag/AgCl/ 3 M KCl/ 1 M LiAc) immersed in 0.1 M HCl, and the impedance spectra were measured across the frequency range of 100 kHz to 10 mHz using a sinusoidal excitation signal (amplitude applied = 10 mV) at the open circuit potential (OCP) of the electrode.

3.2 Part II – Polyaniline-based pH sensors

3.2.1 *Reagents and solutions.*

Aniline was obtained from Fluka Analytical and was distilled before use. Sodium chloride (NaCl) (≥99%) and hydrogen chloride (~37%) were purchased from Sigma Aldrich. Deionised water (ELGA Purelab Ultra, U.K.) was used for all measurements.

3.2.2 *Preparation of electrodes*

Glassy carbon (GC) working electrodes (diameter = 3mm) encased in PVC housing were polished with sandpapers (of grit sizes 600, 1200, 2400 μm), diamond paste (15, 9, 1 μm) and 0.3 μm Al_2O_3 paste. The polished electrodes were ultrasonicated in ethanol and then in deionised water for 5 minutes, respectively.

3.2.3 *Polymerisation by cyclic voltammetry*

In a conventional three-electrode electrochemical cell, consisting of a double junction Ag/AgCl/ 3 M KCl/ 1 M LiAc reference electrode (Metrohm, the Netherlands), a glassy carbon working electrode and a glassy carbon rod as auxiliary electrode in the polymerisation solution (0.05 M aniline + 0.1 M HCl) was purged with N_2 (≥ 99%) for 15 min prior to the polymerisation, after which the nitrogen tubing was lifted above the solution, creating a gas blanket. The deposition of polyaniline on the surface of the working GC (diameter = 3 mm) was performed using cyclic voltammetry, with an Autolab General Purpose Electrochemical System (PGSTAT20, FRA2, AUTOLAB, Eco Chemie, B.V., The Netherlands).

Cyclic voltammetric parameters: potential interval = -0.2 V – +0.82 V, scan rate = 50 mV/s, cycles = 10, 25, 50, 100 and 150. After the polymerisation, the electrodes were dried overnight and conditioned in 0.01 M HCl solution. All electrodes were stored in 0.01 M HCl solution in-between experiments.

3.2.4 Potentiometry and chronoamperometry

Potentiometric measurements were carried out using a multichannel potentiometer (EMF16 Interface, Lawson Laboratories, Inc.) over a concentration range from 10^{-2} to 10^{-5} M HCl, with working SC-ISEs and a reference electrode (a double junction Ag/AgCl/ 3 M KCl/ 1 M LiAc reference electrode). A plot of open circuit potential was then plotted against the logarithm of activity to confirm the proper functioning of H^+-selective polyaniline-based ISEs (> 55 mV/decade corresponding to the theoretical slope).

Chronoamperometric measurements was performed using an Iviumstat (Ivium Technologies, The Netherlands) in a three-electrode cell with a working polyaniline-based ISE, a counter GC rod and a reference electrode, over the concentration range of 10^{-2} to 10^{-5} M.

For both potentiometric and chronoamperometric measurements, the starting solution was 100 mL 0.01 M HCl + 0.1 M NaCl (or 100 mL 0.01 M HCl), gradually diluted with 0.1 M NaCl (or deionised water), respectively. The dilutions were carried out by two Metrohm 700 Dosino units connected to and controlled by a Metrohm 711 Liquino system (Metrohm, the Netherlands). Dilutions were performed in 15 or 20 steps with a 5-min pause between each dilution allowing for equilibration. The dilution system removes 32.4 mL of the electrolyte and replaces it with an equal amount of 0.1 M NaCl (or deionised water) for each dilution, resulting in $\Delta\log a_{H^+} = 0.18$ decades per dilution step.

Sensitivity tests were performed potentiometrically and chronoamperometrically. In an electrochemical cell consisting of a double-junction reference electrode, a working polyaniline-based ISE (and a counter GC rod for chronoamperometric measurements) immersed in 50 mL of 5 mM HCl + 0.1 M NaCl, varying volumes (5 – 40 µL) of 0.1 M HCl + 0.1 M NaCl solution was added with constant stirring.

3.2.5 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy was carried out with an Iviumstat (Ivium Technologies, The Netherlands) in a three-electrode cell containing a working polyaniline-based ISE, a counter GC rod and a reference electrode, immersed in 0.1 M HCl, and the impedance spectra were measured across the frequency range of 100 kHz to 10 mHz using a sinusoidal excitation signal (amplitude = 10 mV) at electrodes' respective open circuit potentials, 0.0 V and 0.2 V.

4 RESULTS & DISCUSSION

4.1 Part I – solid-contact pH-selective electrodes

4.1.1 Potentiometric measurements

Potentiometric calibrations were first performed to ensure the proper functioning of the fabricated SC-ISEs. **Figure 5a** shows the potentiograms of drop-cast H^+-selective ISEs with 10, 15, 20 mC PEDOT(PSS) solid contacts, and a spin-coated H^+-selective ISE with 10 mC PEDOT(PSS) in the step-wise dilution of 0.01 M HCl in the presence of 0.1 M NaCl as the background electrolyte. **Figure 5b** shows the curves of potential against logarithmic activity of H^+. The SC-ISEs with drop-casted ion selective membranes (ISMs) were found to demonstrate a near-Nernstian response where the slopes of potential verses log a_{H+} were 62, 55 and 62 mV/decade for 10, 15 and 20 mC PEDOT(PSS) solid contacts ISEs, respectively. The slight super-Nernstian slopes were observed particularly at lower pH ($< 10^{-3.5}$ M) by 10 and 20 mC PEDOT(PSS) SC-ISEs. The influx of H^+ ions in the diffusion layer at the ion-selective membrane | sample interface could occur at a lower pH range leading to a non-equilibrium of H^+ ions at the boundary.

The spin-coated 10 mC PEDOT(PSS) electrode resulted in a sub-Nernstian response. As seen in **Figure 5b**, it exhibits a poor response against the logarithm of H^+ activity, with a slope of 46 mV/decade; such is the case for other spin-coated electrodes with 1 and 5 mC PEDOT(PSS) SC-ISEs as well (**data not shown in Figure 5**). This could be attributed to the incomplete coverage of the H^+-selective membrane with the spin-coating method, as it gets more difficult to get complete substrate coverage with a low-volume dispense.
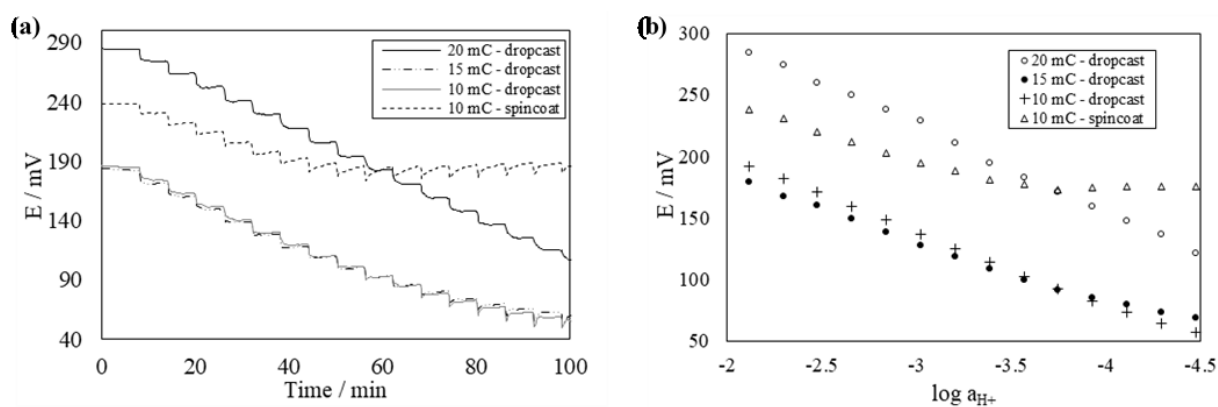

Figure 5. (a) Potentiometric calibration of H^+-selective SC-ISEs with 10, 15 and 20 mC PEDOT(PSS) solid contacts covered with drop-cast ISM and a 10 mC SC-ISE with spin-coated ISM for the 20-step dilution of 0.01 M HCl with 0.1 M NaCl as the background electrolyte. (b) The curve of potential against the logarithmic activity of H^+ for the corresponding electrodes.

4.1.2 Chronoamperometric measurements

A novel signal transduction method based on constant-potential coulometry was introduced recently [2-3, 35-37], where conducting polymers such as PEDOT(PSS) are used as the solid contact (as the ion-to-electron transducer). A constant potential is applied to the electrochemical cell; the chosen potential is dependent on the potential of the reference electrode, the ionic activity in the cell as well as the potential stability window of the conducting polymer [3]. It is expected that the initial equilibration will be reached the fastest when a potential near the open circuit potential (OCP) of the SC-ISE is applied.

Figure 6a shows the chronoamperogram recorded for the drop-cast H^+-selective SC-ISE with 10 mC PEDOT(PSS) solid contact in the stepwise dilution of 0.01 M HCl (with 0.1 M NaCl as the constant ionic background) at constant applied potential. While it can be seen that the current peaks are not readily reproducible with the current response ranging from 0.55 to 1.35 μA, the selectivity of the fabricated electrode is demonstrated with the constant background electrolyte. **Figure 6b** shows the cumulated charge passing through the H^+-selective SC-ISE with 10 mC PEDOT(PSS) solid contact from $10^{-2.1}$ to $10^{-5.7}$ M HCl against time and the curve of charge against the logarithmic activity of H^+ (log a_{H+}) is shown in the inset. As shown in **Figure 6b**, a change of log a_{H+} in 0.18 decade/step was detected, a linear relationship between the total charge and the logarithmic activity of H^+ can be observed.

Figure 7a shows chronoamperometric measurements for drop-cast H^+ selective SC-ISEs with PEDOT(PSS) solid contacts of different charges (1, 5 and 10 mC), for the dilution from $10^{-2.1}$ to $10^{-5.7}$ M HCl without background electrolyte; the first three dilution steps are presented in **Figure 7b**. It can be seen that the thicker the solid-contact film, i.e. the higher the redox
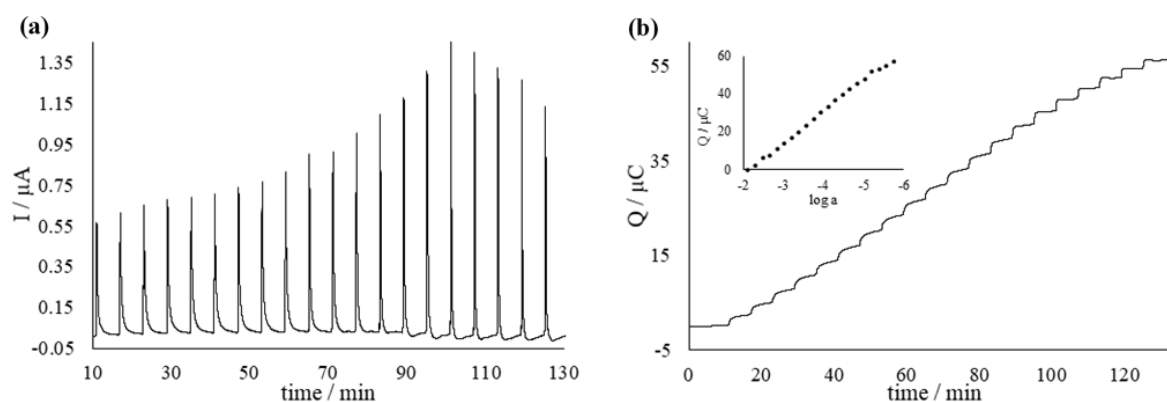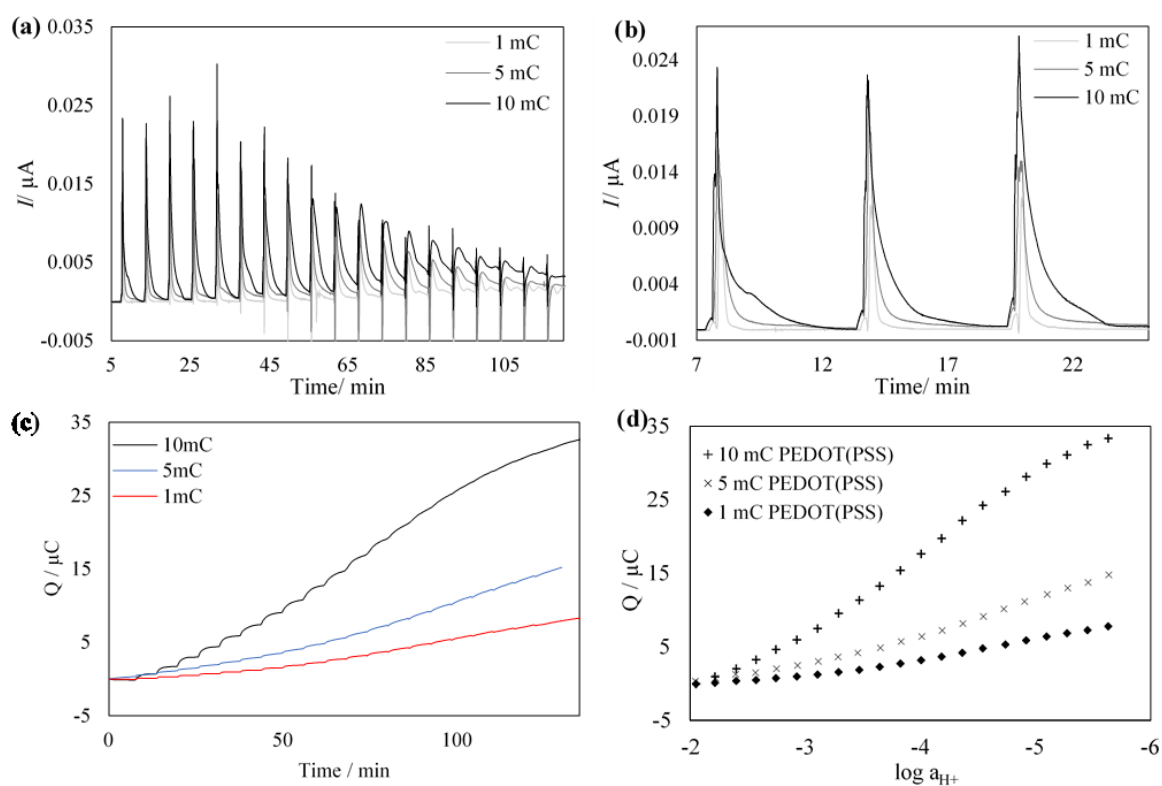

Figure 6. *Chronoamperogram for H^+-selective SC-ISE with 10 mC PEDOT(PSS) solid contact. The starting solution of 10-2 M HCl was diluted in 0.18-decade steps to $10^{-5.7}$ HCl M, with constant ionic background (0.1 M NaCl). (b) Cumulated charge passed through the SC-ISE against time. Cumulated charge against the logarithm of H^+ activity is shown in the inset.*

capacitance, the broader the peak and the longer the equilibration time. At a given potential, the potential of PEDOT(PSS) solid-contact film should be constant as it is dependent on its ionic composition and redox equilibrium, i.e., the ratio between the oxidised and neutral states of PEDOT (PEDOT$^+$/PEDOT^0).

As the overall potential of SC-ISE is held constant, any potential changes at the ISM/solution interface will cause a current to flow through the SC-ISE. This current will cause oxidation/reduction of PEDOT(PSS) that will cause a change in the PEDOT$^+$ to PEDOT^0 ratio. This will gradually change the potential of the PEDOT(PSS) contact to balance the initial potential difference formed at the ISM/solution interface. This results in a relatively long response time as charge-balancing counter-ions are transferred between the conducting polymer solid contact and the solution via the ISM. As the coulometric signal is amplified in SC-ISEs with a higher redox capacitance, this can be utilised in applications where the determination of small changes in primary ion activity is of great significance. **Figures 7c & 7d** shows the curve of total charge against time as well as charge against the logarithm of H$^+$ activity. There is an approximately linear relationship between the charge passed through the SC-ISEs and the logarithmic activity as shown in **Figure 7d**. The slopes of the curve in **Figure**

Figure 7. *Chronoamperograms for H$^+$-selective SC-ISE with 1, 5, and 10 mC PEDOT(PSS) solid contact covered with drop-casted ISMs. The starting solution of $10^{-2.04}$ M HCl was diluted in 0.18-decade steps to $10^{-5.64}$ HCl M, without background electrolyte. (b) Enlargement of the first three dilution steps shown in (a). (c) Cumulated charge passed through the SC-ISEs against time. (d) Cumulated charge against the logarithm of H$^+$ activity of the three SC-ISEs.*

7d calculated to be 2.28, 4.12 and 9.63 μC/ Δlog *a* for 1, 5 and 10 mC PEDOT(PSS) solid contacts, respectively. This indicates that the slope of the response increases with increasing redox capacitance of the solid contact film. It can also be observed that the coulometric response becomes slower at high pH (**Figure 7d).** Less protons are available in solution at a higher pH, which might contribute to this effect.
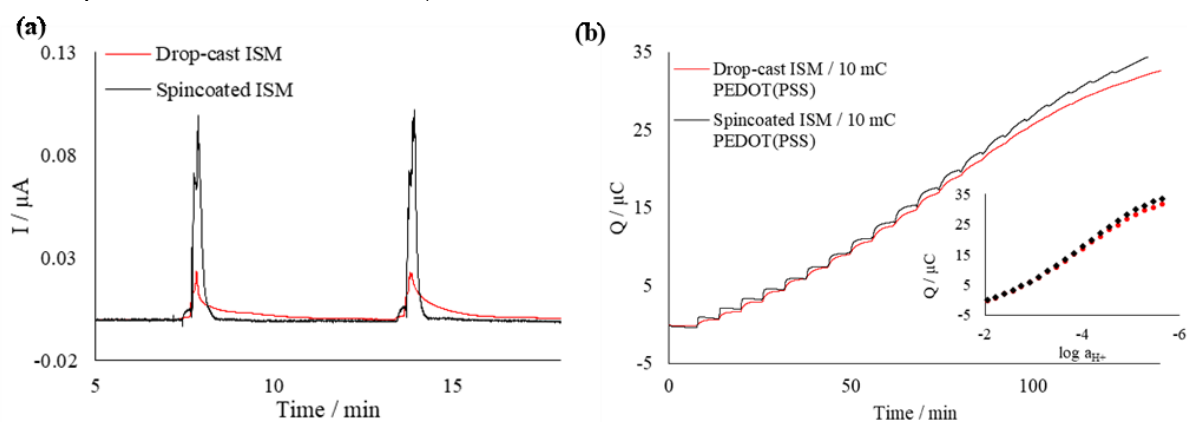
Figure 8a shows the chronoamperograms for the stepwise dilution of 0.01 M HCl with 0.1 M NaCl as the background electrolyte (0.18 decade/step) for the drop-cast H^+-selective SC-ISEs with PEDOT(PSS) solid contacts of different charges (10, 15 and 20 mC). It is shown that the 15 mC PEDOT(PSS) solid-contact ISE required a longer equilibration time and thus resulted in a broader current peak when compared to the 10 mC SC-ISE. However, it is interesting to note that the 20 mC PEDOT (PSS) no longer follows this pattern, this can be seen more clearly in the enlargement of first two dilution steps (**Figure 8b**), where the 20 mC PEDOT(PSS) SC-ISE has a much smaller current response with faster response time compared to its 10 and 15 mC counterparts. Significant background drift is also observed for the 20 mC PEDOT(PSS) SC-ISE as shown in **Figure 8a**. This could be attributed to PEDOT(PSS) solid contact having
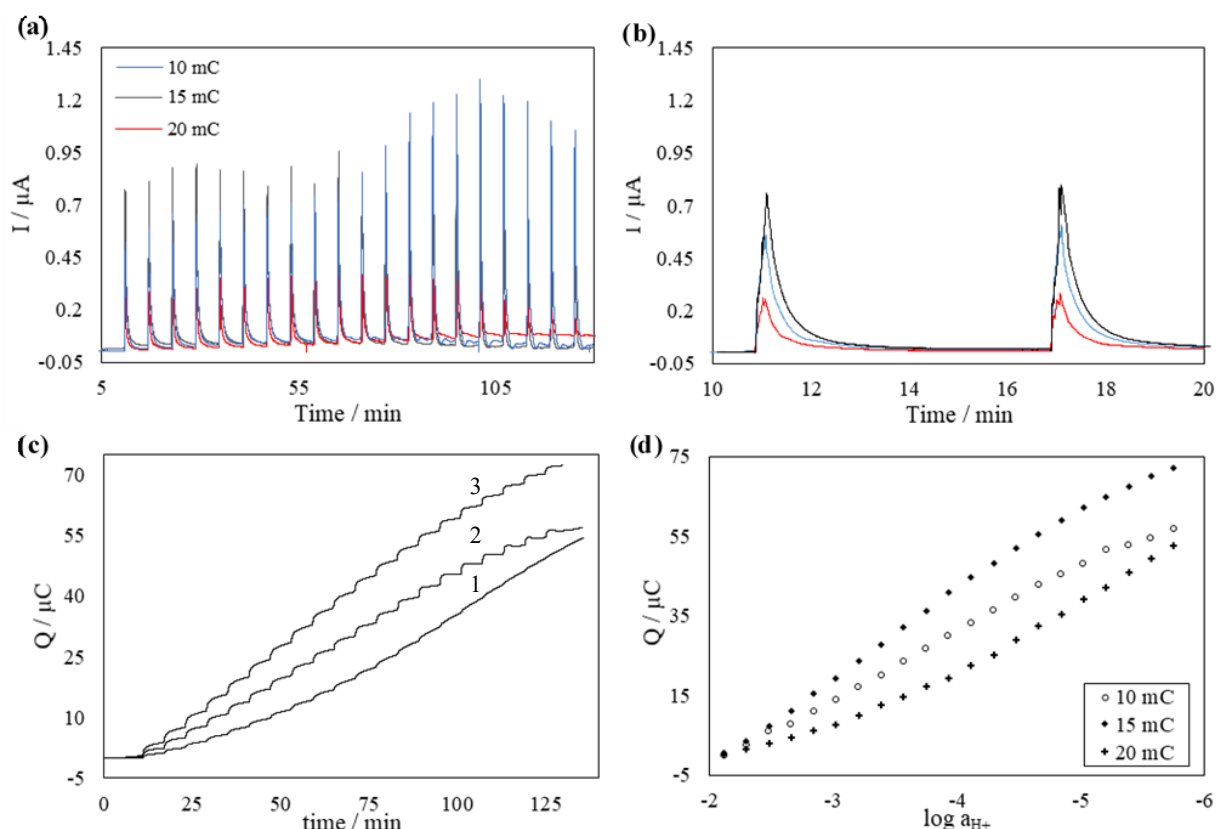
Figure 8. *Chronoamperograms for H^+-selective SC-ISE with 10, 15 and 20 mC PEDOT(PSS) solid contacts and drop-casted ISMs. The starting solution of 10^{-2} M HCl was diluted in 0.18-decade steps to $10^{-5.7}$ HCl M, with constant ionic background (0.1 M NaCl). (b) Enlargement of the first two dilution steps shown in (a). (c) Cumulated charge passed through the SC-ISEs with (1) 20 mC, (2) 10 mC and (3) 15 mC PEDOT(PSS) solid contacts against time. (d) Cumulated charge against the logarithm of H^+ activity of the three SC-ISEs.*

reached its maximum capacitance and a film thickness of 20 mC would actually hinder and dwarf the response. **Figures 8c** shows the cumulated charge (Q) passing through the drop-cast H^+-selective SC-ISEs with 10, 15 and 20 mC PEDOT(PSS) solid contacts against time; and **Figure 8d** shows the curve of charge (Q) against logarithmic activity of H^+ (log a_{H+}) from $10^{-2.1}$ to $10^{-5.7}$ M HCl. As shown in **Figures 8c**, both SC-ISEs of 10 and 15 mC solid contacts were able to detect a change of log a_{H+} in 0.18 decade/step. Their coulometric responses are linearly dependent on the logarithmic activity of H^+ and the slope of the response increases with increasing film thickness as expected (**Figure 8d**). In contrast, a change in H^+ activity with constant ionic background was not well-detected in 20 mC solid contact SC-ISE as evidenced by the much less defined current response steps and the smaller slope of charge against log a_{H+}.

Figure 9a shows the first two dilution peaks of chronoamperograms comparing H^+-selective SC-ISEs with 10 mC PEDOT(PSS) SC-ISEs with spin-coated and drop-cast ion selective membranes, in the stepwise dilution of 0.01 M HCl without background electrolyte (0.18 decade/step). The equilibration time is faster for the spin-coated SC-ISE when compared to the drop-cast SC-ISE. As the spin-coated ion selective membrane is much thinner, there is a faster ion transport between the ISM and the solid-contact layer, resulting in shorter response time and the narrower current peaks. **Figure 9b** shows the coulometric response against time, and the inset shows the curve of charge (Q) against logarithmic activity (log a_{H+}). As shown in **Figure 9b**, both SC-ISEs demonstrated a linear relationship between the charge and the logarithm of activity, and the coulometric response is rather consistent, with slopes of 9.63 and 10.14 µC/ Δlog a for drop-casted ISM and spin-coated ISM, respectively. This shows that the coulometric response (charge) depends mainly on the capacitance of the solid contact, while the response time is influenced by the ion-selective membrane.

Figure 9. *(a) Enlargement of the first two dilution steps in the chronoamperograms for H^+-selective SC-ISE with 1, 5, and 10 mC PEDOT(PSS) solid contact covered with drop-casted ISMs. The starting solution of 10^{-2} M HCl was diluted in 0.18-decade steps to $10^{-5.6}$ HCl M, without background electrolyte. (b) Cumulated charge passed through the SC-ISEs against time and the curve of cumulated charge against the logarithm of H^+ activity in shown in the inset of (b).*

4.1.3 Sensitivity tests

Sensitivity tests were performed chronoamperometrically on the drop-cast 10 mC PEDOT(PSS) H^+-selective SC-ISEs in 50 mL of 5 mM HCl + 0.1 M NaCl with 5-20 µL additions of 0.1 M HCl with 0.1 M NaCl background electrolyte, under constant stirring. **Figure 10** shows (a) the chronoamperometric response, (b) the charge against time, with the enlargement of the first 4 additions as an inset; (c) the integrated charge against the logarithm of activity of H^+, with an enlargement of the first four additions as an inset. Potentiometric measurement was performed under the same conditions, with additions of 15-50 µL additions of 0.1 M HCl + 0.1 M NaCl as shown in **Figure 10d**. The inset of **Figure 10b** demonstrates that the H^+-selective SC-ISE was able to detect additions of 5 µL (0.18 % change in concentration) using the new signal transduction readout method. This implies that this new technique may be applied in combination with ISE to monitor minute concentration changes in solutions. Since the solution is under constant stirring, both the chronoamperometric and potentiometric methods have resulted in a lot of noise (**Figures 10a & 10d**). However, the noise level has been reduced remarkably upon the integration of current over time (**Figure 10c**). In contrast, the signal is less stable in potentiometric measurements (**Figure 10d**).
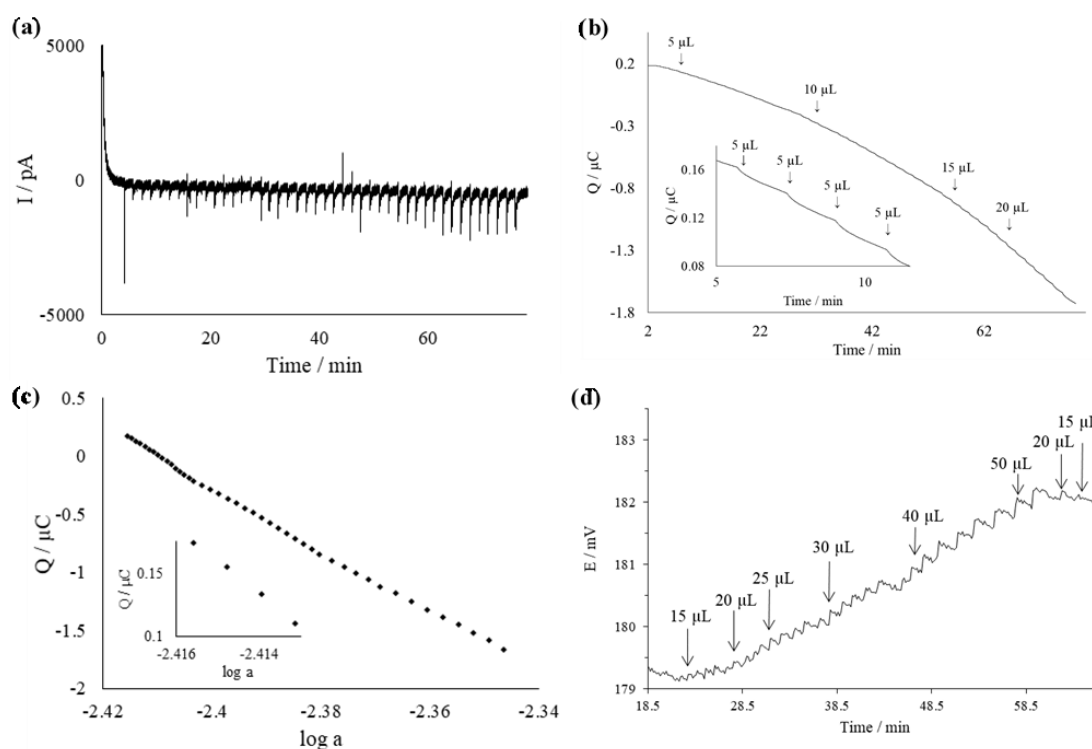

Figure 10. Sensitivity tests for the SC-ISE with 10 mC PEDOT(PSS) solid contact covered with dropcasted ISM in 50 mL 5 mM HCl + 0.1 M NaCl and 5-20 µL additions of 0.1 M HCl with 0.1 M NaCl, under constant stirring. (a) the chronoamperometric response, (b) the charge against time, with the enlargement of the first 4 additions as an inset; (c) cumulated charge against the logarithm of activity of H+, with an enlargement of the first four additions shown in the inset; (d) potentiometric response of the same electrode in 50 mL 5 mM HCl (+ 0.1 M NaCl) with additions of 15-50 µL additions of 0.1 M HCl (+ 0.1 M NaCl).

4.1.4   Electrochemical impedance spectroscopy

Impedance measurements were performed on the H^+-selective SC-ISE with spin-coated ISM and drop-cast ISM in 0.1 M HCl solution at their respective open circuit potentials. The electrochemical impedance spectra are shown in **Figure 11**, with an enlargement of the semi-circles of electrodes with spin-coated ISMs shown in the inset of **Figure 11a**.The diameter of the semi-circle can be used to estimate the bulk resistance of the ion selective membrane; it was found that increasing the thickness of the PEDOT(PSS) solid contact increases the membrane resistance. The spin-coated ISMs are found to have much lower overall membrane resistance (1.5-5.6 kOhm) compared to the drop-cast membranes (65-178 kOhm).

For the spin-coated SC-ISEs, the semi-circle is followed by a low frequency redox capacitive line. The low-frequency redox capacitance of the solid contact film can be estimated by the imaginary impedance at the low frequency region, the SC-ISEs with 1, 5 and 10 mC PEDOT(PSS) covered with thin-layer ISMs have a redox capacitance of 67.3, 130.6 and 233.1 µF. For H^+-SC-ISEs with drop-cast ISMs, the semi-circle is followed by a straight slope, which indicates that H^+-SC-ISEs with drop-cast ISMs could be diffusion limited. This corresponds to the longer equilibration time when using the constant-potential coulometric signal transduction method. As the ion selective membrane was placed on top of the solid-contact layer of the electrode manually, the inconsistency of the bulk resistance could be explained by the experimental uncertainties in the manual drop-casting and spin-coating methods.
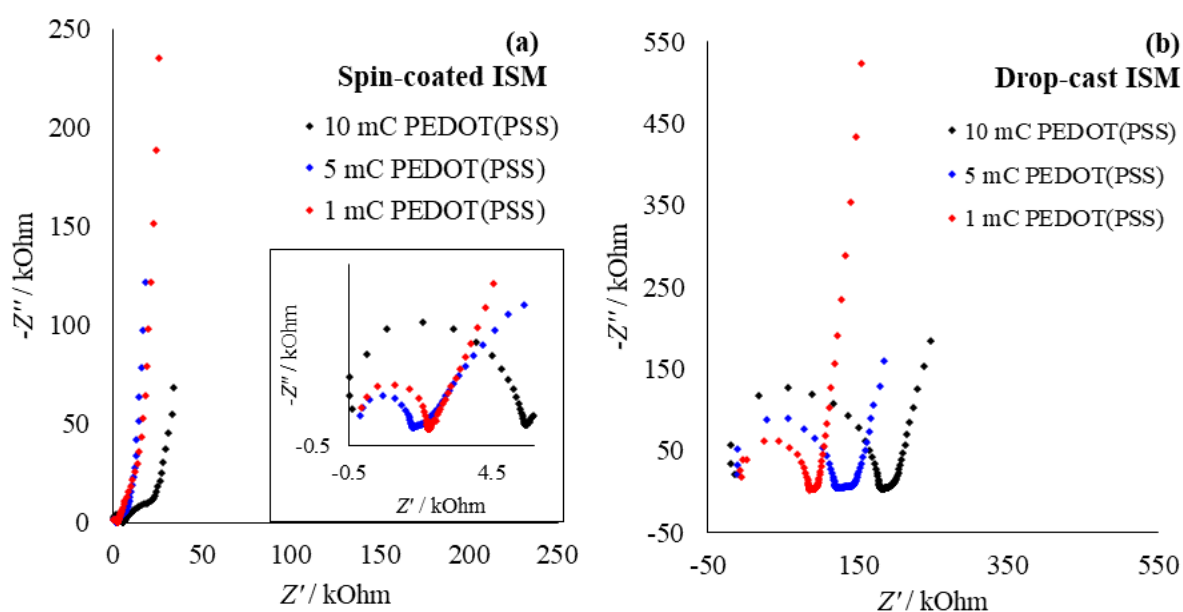
Figure 11. *Impedance spectra of SC-ISEs measured in 0.1 M HCl with 1, 5 and 10 mC PEDOT(PSS) covered with (a) spin-coated ISMs and (b) drop-cast ISMs, in a 3-electrode cell at electrodes' respective OCPs. Frequency range: 100kHz – 10mHz. The enlargement of spectra of PEDOT(PSS) GC-ISEs with spin-coated ISMs are shown in the inset of (a).*

4.2 Part II – Polyaniline-based pH sensors

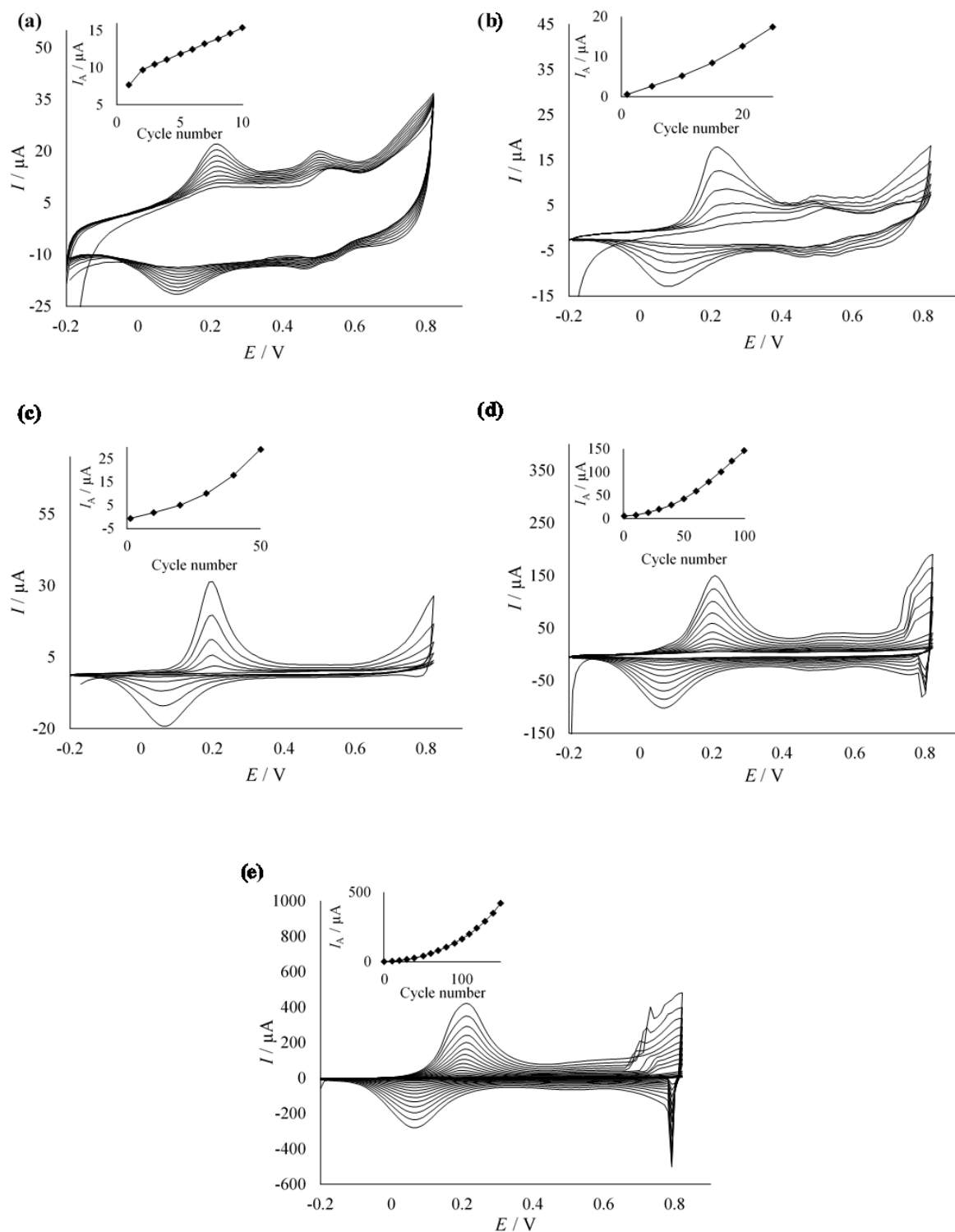### 4.2.1 Polymerisation of polyaniline

Polyaniline was polymerised on bare glassy carbon electrodes (diameter = 3 mm) using cyclic voltammetry with a scan rate of 50 mV/s within the potential interval of -0.2 – 0.82 V. A shiny bluish-green film was obtained after electrodeposition. **Figure 12** shows the cyclic voltammograms (CVs) recorded for the electropolymerisation of PANI(Cl) films of 10, 25, 50 and 100 cycles. The plot of anodic peak current (i_A) against the number of cycles is shown in the inset of the respective CV.

The growth of PANI(Cl) film is rather slow in the first ten cycles (low peak currents), but a considerable increase in current can be seen as the PANI film thickness increases after approximately 20 cycles. The leucoemeraldine base (LEB) to emeraldine salt (ES) transition can be seen at $E_{pa,1}/E_{pc,1} = 200/50$ mV for all electrodes, indicating the successful deposition of the electrically conducting form of PANI. The emeraldine to pernigraniline base transition can be observed at $E > 750$ mV, corresponding to the transition from the second to the third form of PANI as indicated in Figure 10. The ES – PNB transition could result in a minor degradation redox reaction (between hydroquinone and benzoquinone) in the polyaniline film, which could be associated with the second redox couple at $E_{pa,2}/E_{pc,2} = \sim 550/520$ mV [67]. This is seen at 10-, 25- and 100-cycle PANI-ISEs. As the film thickness increases, the degradation peaks and the EB – PNB peaks are significantly smaller in comparison with the first LEB – ES redox pair.

The exponential growth of polyaniline from 50 – 150 cycles can be observed in the insets of **Figure 12**, which correlates well the polymerisation charges obtained from the last cycle of CV as shown in **Figure 13**. The polymerisation charges of PANI-ISE with 10, 25 and 50 cycles are fairly similar in the 0.1 – 0.2 mC range. An increase in polymerisation charges can be observed as the number of cycles of polyaniline increases, with $\sim$ 1 mC for 100-cycle PANI and $\sim$ 3 mC for 150-cycle PANI.

4.2.2 Potentiometric measurements

Same as with SC-ISEs, potentiometric calibrations were first carried out to ensure that the fabricated ISEs are functional. **Figure 14a** shows the potentiograms of H$^+$-selective ISEs with 10, 25, 50, 100 cycles of PANI(Cl) in the gradual dilution of 0.01 M HCl in the presence of 0.1 M NaCl as the background electrolyte (0.18 decade/step). PANI(Cl)-ISEs with 10, 25 and 50 cycles were found to demonstrate a near-Nernstian response from $10^{-2.6}$ M to 10^{-5} M HCl with

Figure 12. *Cyclic voltammograms recorded for the polymerisation of 50 mM polyaniline in 1.0 M HCl on glassy carbon electrode for (a) 10 cycles, (b) 25 cycles (every 5th cycle shown), (c) 50 cycles (every 10th cycle shown), (d) 100 cycles (every 10th cycle shown) and (e) 150 cycles (every 10th cycle shown); v = 50 mV/s. Inset of each CV shows the plot of anodic peak current (iA) against the number of cycles.*
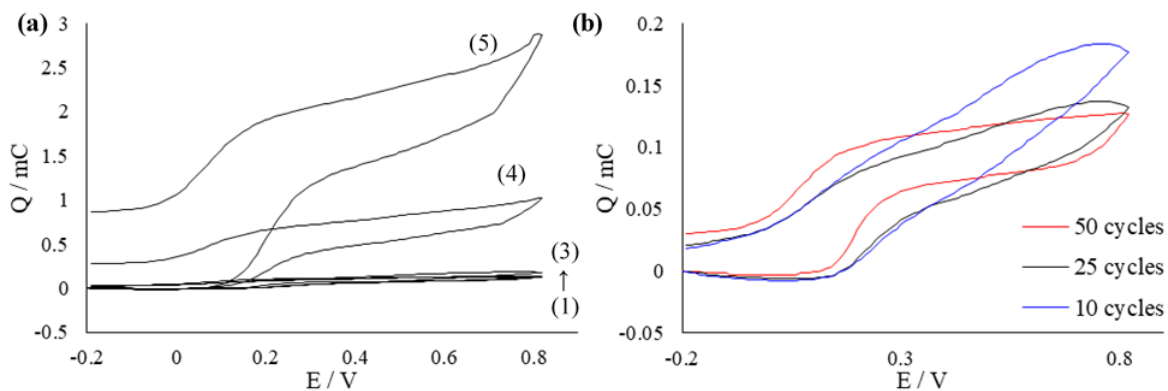
Figure 13. (a) Polymerisation charges of PANI(Cl) electrodes taken from the last CV scan for (1) 10, (2) 25, (3) 50, (4) 100, (5) 150 cycles of PANI. (b) The enlargement of curves (1) – (3) in (a).

slopes of 59.0, 55.8 54.8 and 54.9 mV/ decade for 10, 25, 50 and 100 cycles PANI(Cl)-ISEs, respectively.

Potentiometric calibrations were also carried out on H^+-selective ISEs with 50, 100 and 150 cycles of PANI(Cl) in the stepwise dilution of 0.01 M HCl without any background electrolyte (**Figure 14b**). 50-cycle PANI-ISEs showed a near- to super-Nernstian response (slopes = 59.0-68.0 mV/ decade), with clear and stable stair steps, which is consistent to what Lindfors and Ivaska reported [34].

In contrast, the rest of the ISEs failed to give satisfactory response with slopes of 49.1 and 37.1 mV/ decade for 100- and 150- cycle PANI(Cl)-ISEs, respectively. It is interesting to note the huge difference in slope values for 100-cycle PANI(Cl) in the dilution with and without background electrolyte, indicating its poor reproducibility. As seen in the insets of **Figure 12**, the growth of PANI film increased exponentially from 50-cycle to 150-cycle PANI(Cl)-ISEs (**Insets of Figures 12c – e**). The fairly suppressed Nernstian response shown in these ISEs with
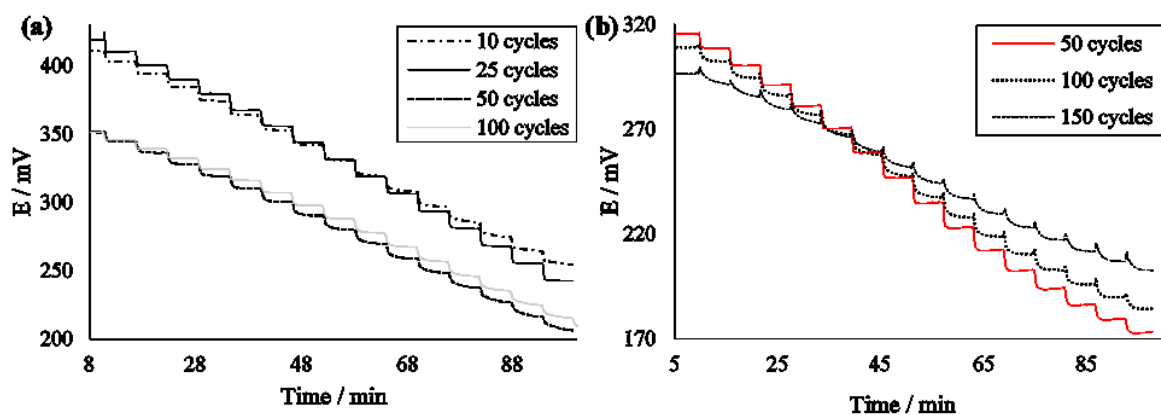

Figure 14. (a) Potentiograms for ISEs with 10, 25, 50 and 100 cycles of polyaniline in the 15-step dilution of 0.01 M HCl (0.18 decade/ step) in presence of 0.1 M NaCl as the background electrolyte. (b) Potentiograms for ISEs with 50, 100 and 150 cycles of polyaniline in the 15-step dilution of 0.01 M HCl (0.18 decade/ step) without any background electrolyte.

relatively thicker PANI membranes might indicate that the sensing membrane has become so thick for 100- and 150- cycle PANI films that it slows down the charge transfer processes of the compensating counter-ions inside the PANI membrane. An increased number of cycles might have induced a change in morphology in PANI (as an exponential growth was observed), which might worsen the ion-to-electron signal transduction.

4.2.3 Chronoamperometric measurements

The constant-potential coulometric signal readout technique was also applied on ISEs with polyaniline membrane. It should be noted that a 15-step dilution was performed for PANI(Cl)-ISE as opposed to 20 steps for PEDOT(PSS) SC-ISEs because preliminary experiments showed that there are little to no coulometric response at lower than 10^{-5} M concentration of HCl. **Figure 15a** shows the chronoamperogram recorded for the H^+-selective ISE covered with 50 cycles of PANI(Cl) in the stepwise dilution of 0.01 M HCl (with 0.1 M NaCl as the constant ionic background) at constant applied potential. **Figure 15b** shows the cumulated charge against time, and the inset shows the cumulated charge against the logarithm of H^+ activity. It
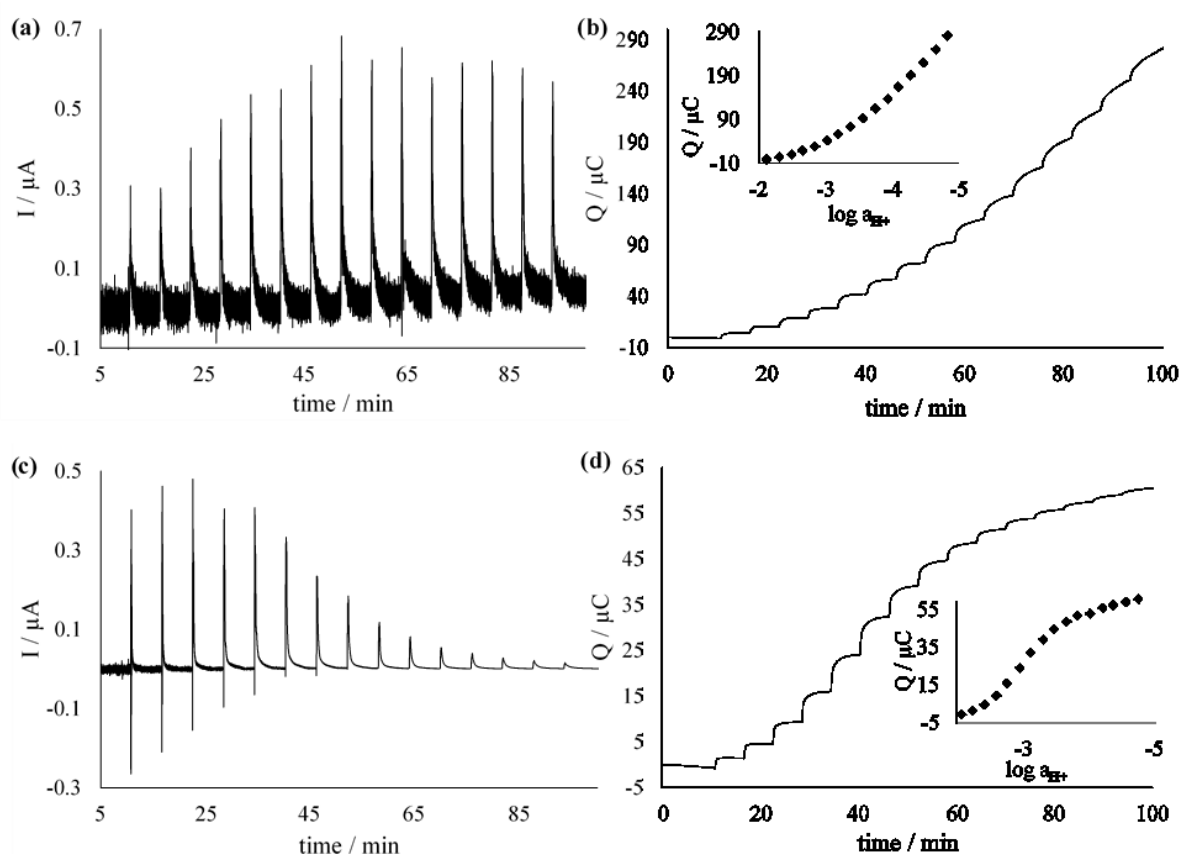
Figure 15. *(a) Chronoamperogram for H^+-selective ISE with 50 cycles PANI in the dilution of 0.01 M HCl in the presence of background electrolyte. (b) the cumulated charge vs time; the inset shows the cumulated charge against the logarithm of H^+ activity. (c) Chronoamperogram showing the gradual dilution of 0.1 M HCl without background electrolyte (0.18 decade / step) for H^+-selective ISE with 50 cycles of PANI. (d) the cumulated charge against time; inset shows the curve of charge against logarithm of H^+ activity.*

can be seen from **Figure 15a** that the current peaks are poorly reproducible ranging from 0.3 to 0.7 µA. Huge noise level is also observed with the presence of ionic background (**Figure 15a**), however, by integrating the current response into charge, the noise level is effectively eliminated. The coulometric response for 50-cycle PANI(Cl)-ISE is shown to be not entirely linear with the logarithm of activity. A linear relationship can be found from $10^{-2.8}$ to $10^{-3.9}$ M HCl, where the coulometric steps are bigger and more prominent (**Figure 15b**).

Figure 15c shows the chronoamperogram recorded for the H^+-selective ISE covered with 50 cycles of PANI(Cl) in the stepwise dilution of 0.01 M HCl without constant ionic background electrolyte; **Figure 15d** shows the cumulated charge against time, and the inset shows the cumulated charge against the logarithm of H^+ activity. The non-linear response can be more clearly seen in 50-cycle PANI(Cl)-ISE in **Figure 15d**. The linearity within this range could be related to LEB – ES redox peak in polyaniline. Unlike PEDOT(PSS) where the cyclic voltammogram is rectangular in shape, polyaniline's cyclic voltammograms contains several peaks. The LEB – ES redox pair at 200/50 mV could be responsible for the highly linear range from $10^{-2.8}$ to $10^{-3.9}$ M HCl. The current response has significantly lower noise level without constant ionic background (**Figure 15c**). This is expected since there's no ion selective membrane, i.e. there is only a layer of conducting polymer, noise level is much higher in presence of 0.1 M NaCl. The integrated coulometric steps have shown to be linearly dependent from $10^{-2.4}$ – $10^{-3.6}$ M HCl (shown in the inset of **Figure 15d)**, with the most pronounced coulometric stair steps.

Figure 16a shows the curves of the integrated charge against time for H^+-selective ISEs comparing polyaniline of different thicknesses (10-, 25-and 50-cycle PANI(Cl)) in the step-wise dilution of 0.01 M HCl under constant ionic background (0.1 M NaCl) with 0.18 decade
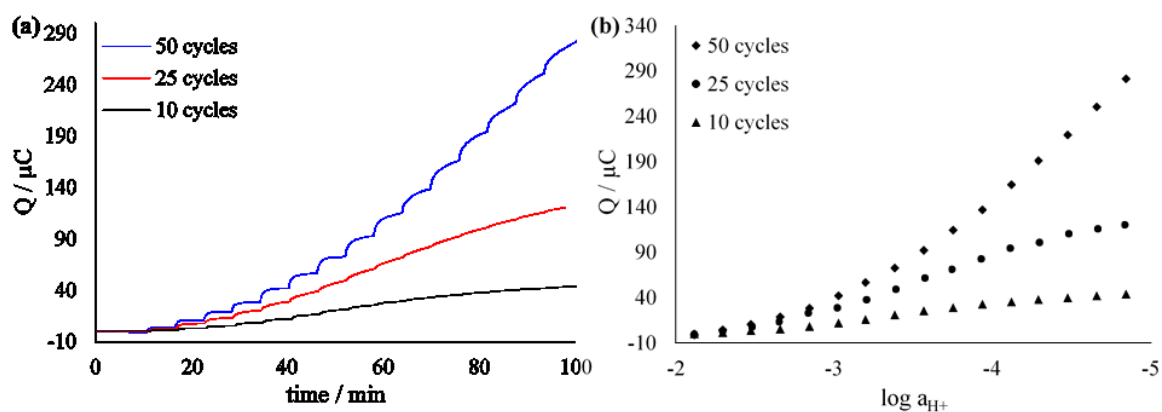
Figure 16. *(a) the curves of the integrated charge against time for H^+-selective ISEs comparing polyaniline of different thicknesses (10-, 25-and 50-cycle PANI(Cl)) in the step-wise dilution of 0.01 M HCl under constant ionic background (0.1 M NaCl) with 0.18 decade per dilution step, **(b)** the charge against logarithm of activity, from $10^{-2.11}$ – $10^{-4.84}$ M.*

per dilution step, whereas **Figure 16b** shows the curve of charge against logarithmic activity, from $10^{-2.11}$ – $10^{-4.84}$ M HCl. Increasing the thickness of polyaniline increases the cumulated charge response as longer equilibration time is needed. It can also be seen that as the thickness of the film increases, the slope of response increases.

4.2.4 Sensitivity tests

Sensitivity tests were performed chronoamperometrically on the H^+-selective ISEs with 50 cycles of PANI(Cl) in 50 mL of 5 mM HCl + 0.1 M NaCl with 10-40 µL additions of 0.1 M HCl with 0.1 M NaCl, under constant stirring. Potentiometric measurements were performed under the same conditions and the addition of 0.1 M HCl (+ 0.1 M NaCl). **Figure 17** shows (a) the curve of integrated charge against time, (b) the enlargement of two 10 µL-additions in (a), (c) the integrated charge against the logarithm of activity of H^+, and (d) the potentiometric response, of the 50-cycle PANI(Cl) H^+-selective ISE. **Figure 17b** demonstrates that the 50-cycle PANI(Cl) H^+-selective SC-ISE was able to clearly detect the additions of 10 µL (0.36 % change in concentration) using the new signal transduction readout method. Since the solution was under constant stirring, potentiometric measurements have resulted in quite a lot of noise (**Figure 17d**). Here it should be noted that sensitivity tests were also attempted with 100-cycle
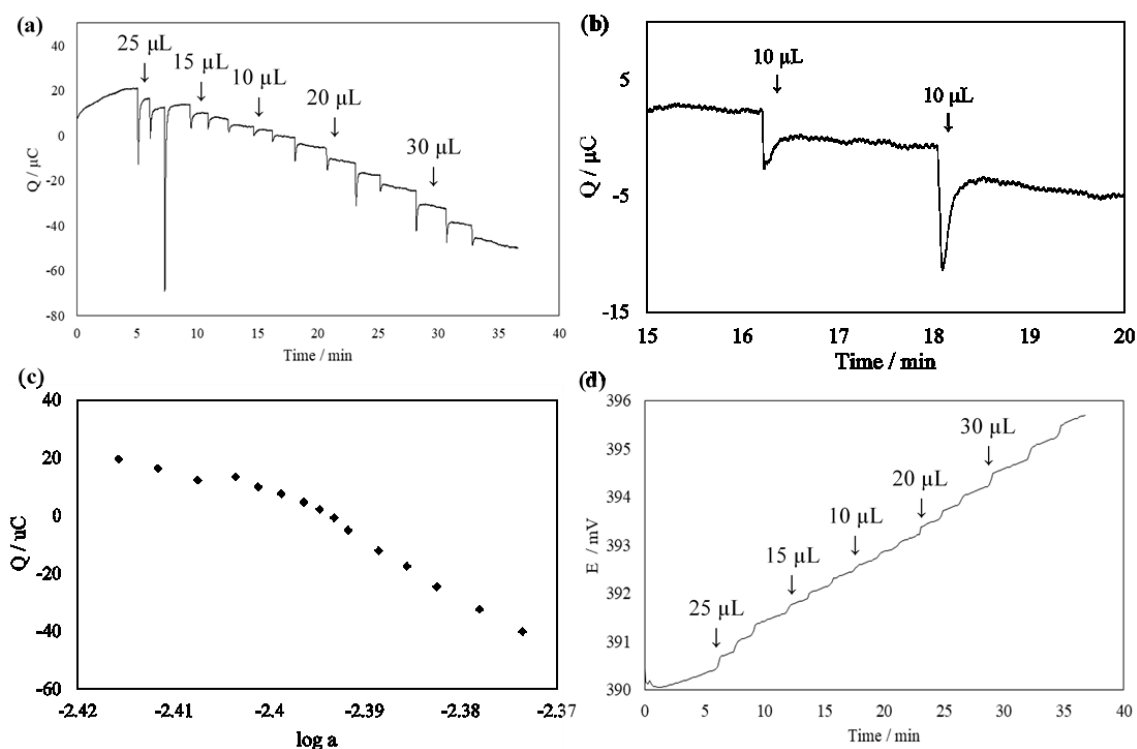
Figure 17. *Sensitivity tests for H^+-selective ISE with 50-cycle PANI(Cl) in 50 mL 5 mM HCl + 0.1 M NaCl and 10-30 µL additions of 0.1 M HCl with 0.1 M NaCl, under constant stirring. (a) the curve of the charge against time, (b) the enlargement of the two 10-µL additions; (c) the curve of cumulated charge against the logarithm of activity of H^+; (d) potentiometric response of the same electrode measured in the same setup.*

PANI(Cl) ISEs but the entire set of experiments could not be performed due to the potential drift in specific electrodes.

Comparing this result to the sensitivity tests of PEDOT(PSS) SC-ISEs, one can say that both types of H^+-selective electrodes can detect very small changes in primary ion concentration in solution, even with the presence of interfering ions. It can also be observed that the potentiometric stair steps in both types of pH sensors in sensitivity tests were not as apparent compared to the coulometric response. The integration of current over time in the novel coulometric transduction method effectively leads to a reduction in noise level. It is interesting to note that PEDOT(PSS) SC-ISEs resulted in potentiometric results with higher noise level; whereas the PANI(Cl)-ISE resulted in less noise but also less clear potentiometric steps upon the addition of 0.1 M HCl (+ 0.1 M NaCl).

4.2.5 *Electrochemical impedance spectroscopy*

Impedance measurements were performed on the PANI-H^+-selective ISEs of different membrane thicknesses (10, 25, 50, 100 and 150 cycles of polyaniline) in 0.1 M HCl solution at their respective open circuit potentials, 0.0 V and 0.2 V. The electrochemical impedance spectra are shown in **Figure 18**. PANI-ISEs have resulted in a tilted straight line in the low frequency region where the impedance can be related to the redox capacitance of PANI. It can be observed that the ISEs' OCPs are quite close to 0.2 – 0.3 in most cases, resulting in rather similar impedance spectra as well. It is interesting to note that measurements done at 0.0 V show significantly lower capacitance compared to the ones done at 0.2 V and OCPs. This correlates well with the CVs (**Figure 12**).

The capacitance increases as the thickness of polyaniline layer increases starting from 50-cycle polyaniline, following the expected pattern. However, 10-, 25- and 50-cycle polyaniline seem to have similarly low capacitance, indicated by the high values ~ 75 – 100 kOhm for measurements done at 0.2 V. Some oligomers could have dissolved after ~ 50 cycles of CV, speeding up the polymerisation process.
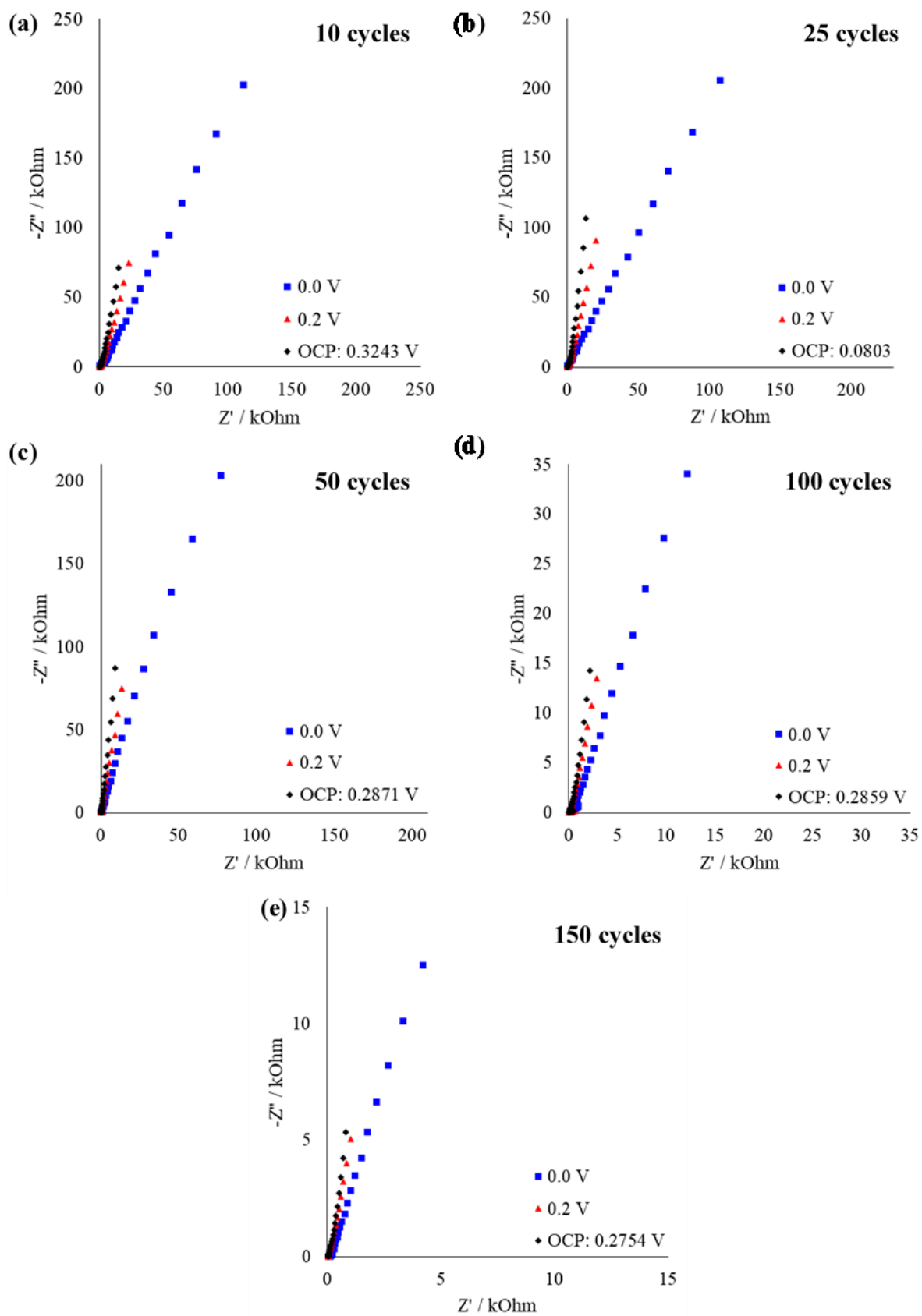
Figure 18. *Impedance spectra of PANI-H⁺ ISE with (a) 10, (b) 25, (c) 50, (d) 100 and (e) 150 cycles, measured in 0.1 M HCl in a 3-electrode cell; frequency range =100kHz – 10mHz, potentials applied = 0.0 V, 0.2 V and OCPs.*

30

5   CONCLUSIONS

In this work, poly(styrene sulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT(PSS)) and chloride-doped polyaniline (PANI(Cl)) were electrochemically synthesised for the construction of H^+-selective electrodes. PEDOT(PSS) was used as the solid-contact (SC) combined with a PVC-based sensing membrane, whereas PANI(Cl) was the sole component of the sensing membrane of the ISEs. In the first case the conducting polymer acted only as ion-to-electron transducer, while in the second case the conducting polymer worked both as ion-to-electron transducer and as sensing membrane.

The analytical performance of solid-contact pH-selective electrodes with thick-layer (drop-casted) and thin-layer (spin-coated) ion-selective membranes was evaluated by the new coulometric signal transduction method. The solid-contact pH sensors were found to have short response time and good selectivity for pH in presence of interfering ions (0.1 M NaCl). ISEs with spin-coated membranes were found to have much lower overall resistance than the drop-casted membranes, and therefore a faster response in the coulometric signal readout. This could be associated with a faster ion transport between the sensing membrane and the PEDOT(PSS) solid contact with a thinner ISM, which is consistent with what has been reported in the literature so far [8,9]. However, initial potentiometric measurements have shown that reproducibility was an issue with spin-coated membranes due to the potential incomplete coverage of ion-selective membrane. Thus, care should be taken to ensure a complete coverage on the surface of the electrode.

The influence of thickness of conducting polymers on the performance of H^+-selective electrodes were investigated. PEDOT(PSS)-based solid-contact with polymerisation charges 1, 5, 10, 15 and 20 mC were investigated with or without background electrolyte. Results showed that up to 15 mC PEDOT(PSS), the thicker the solid-contact layer, the longer the equilibration time. Thus, a broader and larger current peak was recorded, amplifying the analytical signal. However, 20 mC solid contact did not follow the same pattern, with a smaller current peak and faster response time.   After approximately 3 weeks of use and storage, the detachment of 20 mC PEDOT(PSS) layer from GC electrode surface was observed; thus, its coulometric response could be related to the maximum capacitance of PEDOT(PSS) film being reached at 20 mC and thus hindering both the potentiometric and coulometric response.

Polyaniline-based H^+-selective ISEs with 10, 25, 50, 100 and 150 cycles of polyaniline were prepared, and their performance was evaluated with and without background electrolyte. It was

found that H$^+$-selective electrodes with 10, 25 and 50 cycles of polyaniline had similarly low polymerisation charges and capacitances; whereas from 50 cycles onwards, the thicker the polyaniline film, the higher the polymerisation charge and the higher the capacitance. It is interesting to note that the coulometric charge vs pH curve is non-linear for the PANI(Cl)-ISEs. This could be related to the fact that chloride doped polyaniline acts as the only component of the ion sensing membrane, the response of the electrode is influenced by the PANI film. From the CV of polyaniline, there are at least one pair of redox peaks, meaning that the redox capacitance of polyaniline is dependent on the potential. The coulometric response will also be dependent on the potential. On the other hand, cyclic voltammogram of PEDOT solid contact is almost rectangular in shape, meaning its redox capacitance is relatively constant over a wide potential range. The linear proportion of the PANI(Cl)-ISE could be associated with the conducting leucoemerladine to emeraldine salt peaks, which can be found at around 200/50 mV/s. Similarly, interfering ions has a noticeable effect on the chronoamperometric response PANI(Cl)-ISEs. One can utilise this information to fabricate sensors for the continuous monitoring of very minute changes in pH.

Sensitivity tests were performed using a 10 mC PEDOT(PSS) SC-ISE covered with a drop-casted ISM and a 50-cycle PANI(Cl)-ISE using the novel coulometric transduction method. This new method was able to detect a 0.18 % concentration change for PEDOT(PSS) SC-ISE and a 0.36% change in concentration for PANI(Cl)-ISE, corresponding to Δ pH = 0.001 and 0.002, respectively.

The presented results indicate the potential of the newly developed coulometric transduction readout method in practical applications where minute concentration monitoring is needed. Solid-state ion-selective electrodes utilising PEDOT(PSS) and polyaniline have the merits of simple construction, low cost with excellent electronic and ionic conductivities. However, future research is required to improve the electrode's background drift as well as the reproducibility.

6 REFERENCES

[1] Hupa, E., Vanamo, U., & Bobacka, J. (2015). Novel ion-to-electron transduction principle for solid-contact ISEs. *Electroanalysis, 27*(3), 591-594.

[2] Vanamo, U., Hupa, E., Yrjänä, V., & Bobacka, J. (2016). New signal readout principle for solid-contact ion-selective electrodes. *Analytical Chemistry, 88*(8), 4369-4374.

[3] Bobacka, J., Ivaska, A., & Lewenstam, A. (2008). Potentiometric ion sensors. *Chemical Reviews, 108*(2), 329-351.

[4] Mavrič, T., Benčina, M., Imani, R., Junkar, I., Valant, M., Kralj-Iglič, V., *et al.* (2018). Chapter three - electrochemical biosensor based on TiO_2 nanomaterials for cancer diagnostics. *Advances in Biomembranes and Lipid Self-Assembly, 27*(2018), 63-105.

[5] Smolinska-Kempisty, K., Ahmad, O. S., Guerreiro, A., Karim, K., Piletska, E., & Piletsky, S. (2017). New potentiometric sensor based on molecularly imprinted nanoparticles for cocaine detection. *Biosensors and Bioelectronics, 96*(2017), 49-54.

[6] Ceresa, A., Bakker, E., Hattendorf, B., Günther, D., & Pretsch, E. (2001). Potentiometric polymeric membrane electrodes for measurement of environmental samples at trace levels: New requirements for selectivities and measuring protocols, and comparison with ICPMS. *Analytical Chemistry, 73*(2), 343-351.

[7] Bobacka, J. (1999). Potential stability of all-solid-state ion-selective electrodes using conducting polymers as ion-to-electron transducers. *Analytical Chemistry, 71*(21), 4932-4937.

[8] Jarolímová, Z., Han, T., Mattinen, U., Bobacka, J., & Bakker, E. (2018). Capacitive model for coulometric readout of ion-selective electrodes. *Analytical Chemistry*, *90*(14), 8700-8707.

[9] Han, T., Vanamo, U., & Bobacka, J. (2016). Influence of electrode geometry on the response of Solid-Contact Ion-Selective electrodes when utilizing a new coulometric signal readout method. *ChemElectroChem, 3*(12), 2071-2077.

[10] Si, P. & Bakker, E. (2009). Thin layer electrochemical extraction of non-redoxactive cations with an anion-exchanging conducting polymer overlaid with a selective membrane. *Chemical Communications, 2009*(35), 5260-5262.

[11] Pławińska, Ż., Michalska, A., & Maksymiuk, K. (2016). Optimization of capacitance of conducting polymer solid contact in ion-selective electrodes. *Electrochimica Acta, 187*(2016), 397-405.

[12] Abramova, N., Moral-Vico, J., Soley, J., Ocaña, C., & Bratov, A. (2016). Solid contact ion sensor with conducting polymer layer copolymerized with the ion-selective membrane for determination of calcium in blood serum. *Analytica Chimica Acta, 943*(2016), 50-57.

[13] Liu, C., Jiang, X., Zhao, Y., Jiang, W., Zhang, Z., & Yu, L. (2017). A solid-contact Pb^{2+}-selective electrode based on electrospun polyaniline microfibers film as ion-to-electron transducer. *Electrochimica Acta, 231*(2017), 53-60.

[14] Hussain, R., Khan, M. Q., & Khan, A. A. (2019). Electrochemical sensing of Pb^{2+} ion in water by ion selective membrane electrode based on Polypyrrole titanium(IV)sulphosalicylo phosphate cation exchange nanocomposite. *Groundwater for Sustainable Development, 8*, 216-225.

[15] Şahutoğlu, A. K., & Kaya, İ. (2019). Synthesis and a new mercury (II) ion sensor application of conductive polymer containing rhodamine B. *Reactive and Functional Polymers, 141*(2019), 50-57.

[16] Hulanicki, A., Glab, S., & Ingman, F. (1991). Chemical sensors: Definitions and classification. *Pure and Applied Chemistry, 63*(9), 1247-1250.

[17] Young, C. C. (1997). Evolution of blood chemistry analyzers based on ion selective electrodes. *Journal of Chemical Education, 74*(2), 177.

[18] Buck, R. P., & Lindner, E. (1994). Recommendations for nomenclature of ionselective electrodes (IUPAC recommendations 1994). *Pure and Applied Chemistry, 66*(12), 2527-2536.

[19] Cattrall, R. W., & Freiser, H. (1971). Coated wire ion-selective electrodes. *Analytical Chemistry, 43*(13), 1905-1906.

[20] Bobacka, J. (2006). Conducting polymer-based solid-state ion-selective electrodes. *Electroanalysis, 18*(1), 7-18.

[21] Nikolskii, B. P., & Materova, E.A. (1985). Solid Contact in Membrane Ion-Selective Electrodes. *Ion-Selective Electrode Reviews, 7*(1985), 3-39.

[22] Bobacka, J., Ivaska, A., & Lewenstam, A. (2003). Potentiometric ion sensors based on conducting polymers. *Electroanalysis, 15*(5), 366-374.

[23] Jiang, C., Yao, Y., Cai, Y., & Ping, J. (2019). All-solid-state potentiometric sensor using single-walled carbon nanohorns as transducer. *Sensors and Actuators B: Chemical, 283*(2019), 284-289.

[24] Cattrall, R. W. (1997). *Chemical sensors* (1st ed.). Oxford: Oxford University Press.

[25] Armstrong, R.D., & Todd, M. (1987). The role of PVC in ion selective electrode membranes. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 237*(2), 181-185.

[26] Zareh, M. M. (2012). Plasticizers and Their Role in Membrane Selective Electrodes. *Recent Advances in Plasticizers*. London: InTech.

[27] Mikhelson, K. N. (2013). *Ion-selective electrodes*. Berlin: Springer.

[28] Ito, T., Shirakawa, H., & Ikeda, S. (1974). Simultaneous polymerization and formation of polyacetylene film on the surface of concentrated soluble ziegler-type catalyst solution. *Journal of Polymer Science: Polymer Chemistry Edition, 12*(1), 11-20.

[29] Le, T., Kim, Y., & Yoon, H. (2017). Electrical and electrochemical properties of conducting polymers. *Polymers, 9*(4), 150.

[30] Su, W. P., Schrieffer, J. R., & Heeger, A. J. (1979). Solitons in polyacetylene. *Physical Review Letters, 42*(25), 1698-1701.

[31] Cadogan, A., Gao, Z., Lewenstam, A., Ivaska, A., & Diamond, D. (1992). All-solid-state sodium-selective electrode based on a calixarene ionophore in a poly(vinyl chloride) membrane with a polypyrrole solid contact. *Analytical Chemistry, 64*(21), 2496-2501.

[32] Masalles, C., Borrós, S., Viñas, C., & Teixidor, F. (2002). Simple PVC–PPy electrode for pH measurement and titrations. *Analytical and Bioanalytical Chemistry, 372* (4), 513-518.

[33] Zhang, X., Ogorevc, B., & Wang, J. (2002). Solid-state pH nanoelectrode based on polyaniline thin film electrodeposited onto ion-beam etched carbon fiber. *Analytica Chimica Acta ,452*(1), 1-10.

[34] Lindfors, T., & Ivaska, A. (2002). pH sensitivity of polyaniline and its substituted derivatives. *Journal of Electroanalytical Chemistry, 531*(1), 43-52.

[35] Lindfors, T., & Ivaska, A. (2002). Potentiometric and UV–vis characterisation of N-substituted polyanilines. *Journal of Electroanalytical Chemistry, 535*(1), 65-74.

[36] Huang, W., Humphrey, B. D., & MacDiarmid, A. G. (1986). Polyaniline, a novel conducting polymer. Morphology and chemistry of its oxidation and reduction in aqueous electrolytes. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases, 82*(8), 2385-2400.

[37] Letheby, H. (1862). XXIX.-On the production of a blue substance by the electrolysis of sulphate of aniline. *Journal of the Chemical Society, 15*, 161-163

[38] Lindfors, T., & Ivaska, A. (2001). Calcium-selective electrode based on polyaniline functionalized with bis[4-(1,1,3,3-tetramethylbutyl)phenyl]phosphate. *Analytica Chimica Acta, 437(2*), 171-182.

[39] Lindfors, T., Szücs, J., Sundfors, F. & Gyurcsányi., R. E. (2010). Polyaniline Nanoparticle-Based Solid-Contact Silicone Rubber Ion-Selective Electrodes for Ultratrace Measurements. *Analytical Chemistry, 82*(22), 9425-9432.

[40] Quillard, S., Berrada, K., Louarn, G., Lefrant, S., Lapkowski, M. & Pron, A. (1995). In-Situ Raman-Spectroscopic Studies of The Electrochemical-Behavior Of Polyaniline. *New journal of chemistry, 19*(4), 365-374.

Huang, W., Humphrey, B. D., & MacDiarmid, A. G. (1986). Polyaniline, a novel conducting polymer. Morphology and chemistry of its oxidation and reduction in aqueous electrolytes. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases, 82*(8), 2385-24.

[41] Kilmartin, P. A., & Wright, G. A. (1999). Photoelectrochemistry and spectroscopy of substituted polyanilines. *Synthetic Metals, 104*(3), 145-156.

[42] Yam, P. (1997). Plastics Get Wired. *Scientific American, Special Edition* (1), 90-97.

[43] de Leon, A., & Advincula, R. C. (2014). Chapter 11 - Conducting Polymers with Superhydrophobic Effects as Anticorrosion Coating. *Intelligent coatings for corrosion control* (1st ed.). Oxford: Elsevier.

[44] Han, W., Park, M., Chung, K., Cho, D., & Hong, T. (2001). All Solid State Hydrogen Ion Selective Electrode Based on a Tribenzylamine Neutral Carrier in a Poly(vinyl chloride) Membrane with a Poly(aniline) Solid Contact. *Electroanalysis, 13*(11), 955-959.

[45] Bobacka, J., Lindfors, T., McCarrick, M., Ivaska, A., & Lewenstam, A. (1995). Single-piece all-solid-state ion-selective electrode. *Analytical Chemistry, 67*(20), 3819-3823.

[46] Lindfors, T., Bobacka, J., Lewenstam, A., & Ivaska, A. (1996). Impedance spectroscopic study on single-piece all-solid-state calcium-selective electrode based on polyaniline. *The Analyst, 121*(12), 1823-1827.

[47] Lindfors, T., Sjöberg, P., Bobacka, J., Lewenstam, A., & Ivaska, A. (1999). Characterization of a single-piece all-solid-state lithium-selective electrode based on soluble conducting polyaniline. *Analytica Chimica Acta, 385*(1), 163-173.

[48] Lindfors, T., & Ivaska, A. (2000). All-solid-state calcium-selective electrode prepared of soluble electrically conducting polyaniline and di(2-ethylhexyl)phosphate with ETH1001 as neutral carrier. *Analytica Chimica Acta, 404*(1), 101-110.

[49] Lindfors, T., & Ivaska, A. (2000). All-solid-state calcium-selective electrode prepared of soluble electrically conducting polyaniline and di(2-ethylhexyl)phosphate with tetraoctylammonium chloride as cationic additive. *Analytica Chimica Acta, 404*(1), 111-119.

[50] Lindfors, T., Kvarnström, C., & Ivaska, A. (2002). Raman and UV–vis spectroscopic study of polyaniline membranes containing a bulky cationic additive. *Journal of Electroanalytical Chemistry, 518*(2), 131-138.

[51] Lövenich, W. (2014). PEDOT-properties and applications. *Polymer Science Series C, 56*(1), 135-143.

[52] Kirchmeyer, S., & Reuter, K. (2005). Scientific importance, properties and growing applications of poly(3,4-ethylenedioxythiophene). *Journal of Materials Chemistry, 15*(21), 277-288.

[53] Søndergaard, R., Hösel, M., Angmo, D., Larsen-Olsen, T. T., & Krebs, F. C. (2012). Roll-to-roll fabrication of polymer solar cells. *Materials Today, 15*(1-2), 36-49.

[54] Vázquez, M., Bobacka, J., Ivaska, A., & Lewenstam, A. (2002). Influence of oxygen and carbon dioxide on the electrochemical stability of poly(3,4-ethylenedioxythiophene) used as ion-to-electron transducer in all-solid-state ion-selective electrodes. *Sensors and Actuators B: Chemical, 82*(1), 7-13.

[55] Lindfors, T., Sundfors, F., Höfler, L., & Gyurcsányi, R. E. (2011). The Water Uptake of Plasticized Poly(vinyl chloride) Solid-Contact Calcium-Selective Electrodes. *Electroanalysis, 23*(9), 2156-2163.

[56] Lindfors, T. (2009). Light sensitivity and potential stability of electrically conducting polymers commonly used in solid contact ion-selective electrodes. *Journal of Solid State Electrochemistry, 13*(1), 77-89.

[57] Bobacka, J., Gao, Z., Ivaska, A., & Lewenstam, A. (1994). Mechanism of ionic and redox sensitivity of p-type conducting polymers: Part 2. experimental study of polypyrrole. *Journal of Electroanalytical Chemistry, 368*(1), 33-41.

[58] Lewenstam, A., Bobacka, J., & Ivaska, A. (1994). Mechanism of ionic and redox sensitivity of p-type conducting polymers: Part 1. theory. *Journal of Electroanalytical Chemistry, 368*(1), 23-31.

[59] Sawyer, D. T., Sobkowiak, A., & Roberts, J. L. (1995). *Electrochemistry for chemists* (2nd ed.). New York: Wiley.

[60] Inzelt, G. (2012). *Conducting polymers. A new era in electrochemistry* (2nd Ed.). Berlin: Springer.

[61] Gvozdenović, M. M., Jugović, B. Z., Stevanović, J. S., & Grgur, B. N. (2014). Electrochemical synthesis of electroconducting polymers. *Hemijska Industrija, 68*(6), 673-684.

[62] Rahman, M. A., Kumar, P., Park, D. S., & Shim, Y. B. (2008). Electrochemical Sensors Based on Organic Conjugated Polymers. *Sensors, 8*(1), 118–141.

[63] Bobacka, J., Grzeszczuk, M., & Ivaska, A. (1992). Electrochemical study of poly(3-octylthiophene) film electrodes. impedance of the polymer film semiconductor-electrolyte interface. *Electrochimica Acta*, *37*(10), 1759-1765.

[64] Bobacka, J., Grzeszczuk, M., & Ivaska, A. (1997). Electron transfer at conducting polymer film electrodes: Mechanism and kinetics of ferrocene oxidation at poly(3-octylthiophene). *Journal of Electroanalytical Chemistry*, *427*(1), 63-69.

[65] Bobacka, J., Lewenstam, A., & Ivaska, A. (2000). Electrochemical impedance spectroscopy of oxidized poly(3,4-ethylenedioxythiophene) film electrodes in aqueous solutions. *Journal of Electroanalytical Chemistry, 489*(1), 17-27.

[66] Sundfors, F., Bobacka, J., Ivaska, A., & Lewenstam, A. (2002). Kinetics of electron transfer between $Fe(CN)_6^{3-}/^{4-}$ and poly(3,4-ethylenedioxythiophene) studied by electrochemical impedance spectroscopy. *Electrochimica Acta, 47*(13), 2245-2251.

[67] Arsov, L. D., Plieth, W., & Koßmehl, G. (1998). Electrochemical and Raman spectroscopic study of polyaniline; influence of the potential on the degradation of polyaniline. *Journal of Solid State Electrochemistry, 2*(5), 355-361.