



# Electrocoating Polypyrrole on Gold-Wire Electrode as Potential Mediator Membrane Candidate for Anionic Surfactant Electrode Sensor



Abdul Haris Watoni<sup>a,1,\*</sup>, Indra Noviandri<sup>b,2</sup>, Muhammad Nurdin<sup>a,3</sup>,  
 La Ode Ahmad Nur Ramadhan<sup>a,4,\*</sup>

<sup>a</sup> Department of Chemistry, Faculty of Mathematics and Natural Sciences, Halu Oleo University, Kendari, Indonesia

<sup>b</sup> Department of Chemistry, Faculty of Mathematics and Natural Sciences, Bandung Institute of Technology, Bandung, Indonesia

\* Author emails: (1,\*) [ahwatoni@gmail.com](mailto:ahwatoni@gmail.com); (2) [innov@chem.itb.ac.id](mailto:innov@chem.itb.ac.id); (3) [mnurdin06@gmail.com](mailto:mnurdin06@gmail.com); (4) [ramadhan306@gmail.com](mailto:ramadhan306@gmail.com)

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## Abstract

The development of polypyrrole as a potential mediator membrane candidate for sodium dodecyl sulfate (SDS) sensor electrode has been investigated. The polypyrrole membrane was synthesized electrochemically from the pyrrole and coated at the surface of a 1.0 mm diameter of the gold-wire electrode. Electropolymerization of pyrrole and coating of the polypyrrole produced was performed by cyclic voltammetry technique in the electrochemical cell containing supporting electrolyte of 0.01 M NaClO<sub>4</sub> with an optimum potential range of -0.9 V–1.0 V, the scanning rate of 100 mV/s, an electric current of 2 mA, and running of potential scanning of 10 cycles. By using the similar optimal parameters of cyclic voltammetry, electropolymerization of 0.01 M pyrrole solution containing 0.001 M SDS also produces a polypyrrole membrane coated at the gold-wire electrode surface. These coated electrodes have the potential response-ability toward DS<sup>-</sup> anions in the concentration range of 10<sup>-7</sup> M–10<sup>-5</sup> M with a limit of detection of 10<sup>-7</sup> M and sensitivity of electrode of 9.9 mV/decade. This finding shows that the SDS solution's role is as supporting electrolyte and also as a source of DS<sup>-</sup> dopant during the pyrrole electropolymerization processes. Dopants are trapped in the polymer membrane during the electrochemical formation of polypyrrole and role as ionophores for DS<sup>-</sup> anion in the analyte solution. A potential response to the electrode phenomena is excellent basic scientific information for further synthesis of conducting polymer and development of conducting polymer-coated wire electrode model, especially in the construction of ion-selective electrode (ISE) for the determination of anionic surfactants with those models.

## 1. Introduction

Conducting polymers is a unique and essential new material because of its electrical, optical, and chemical properties. The electrical conductivity of the materials can be increased from semiconductors, such as to the properties of metals, by doping with appropriate dopants [1]. The advantage of conducting polymer over a new concept of the charged material transport mechanism. The study of conducting polymer aims to modify polymers to upgrade their application, primarily based on their morphology and electrical properties.

Polypyrrole (PPy), a type of conducting polymer, has ionic and electronic conductivities [2, 3, 4, 5]. The electrical conductivity of polypyrrole is one of the essential properties for the development of electrochemical analysis techniques. Based on electrical conductivity, polypyrrole is studied in many fields of study. These conducting polymers have environment stability [6, 7], electrolytic activity [8], and can be easily synthesized [9]. In the electrochemical applications, polypyrrole is developed as electrode sensing material [10], catalyst in fuel cell [11], supercapacitor [12], and solar cell [13].

The analyte potentiometrically determines one kind of analysis of the electrochemical method. This determination uses indicator electrodes to respond to analyte ions and reference electrodes selectively. The indicator electrode is equipped with a polymer membrane as an ionic exchange mediator between analyte ions with ionophore ions trapped in the membrane. The ionic exchange equilibrium reaction takes place at the membrane interface and analyte solution. One indicator electrode studied today is the ion-selective electrode (ISE) of the coated wire electrode model. The coated wire electrode has a small diameter of 0.5–2.0 mm so that it can be applied on an intracellular scale of determinations [14]. With the size of the electrode, the determination of analyte ions using coated wire electrodes can be carried out thrifter than that of using a tube electrode model. Based on the electric and ionic conductivity properties of conducting polymer, it is expected that ISE constructed from conducting a polymer-coated wire model has better performance than the other models [15, 16].

The conducting polymer included polypyrrole, can be synthesized easily by chemical and electrochemical methods [17]. The deposition and coating of polypyrrole at the metal wire electrode surface were carried out during the pyrrole electropolymerization by cyclic voltammetry technique [18]. Using this technique, the electron transfer process during the pyrrole electropolymerization and the resulting polypyrrole membrane coating can be studied from the indicated cyclic voltammograms. Pyrrole electropolymerization and the resulting polypyrrole coating must be carried out within a specific range of scanning potential, scanning rate, and certain cycles. Morphology and characteristics of the polymer depend on trapped dopants, the solution acidity, existing supporting electrolytes, and the concentration of pyrrole monomers applied during the electropolymerization processes [15, 19, 20]. Those factors influence the potentiometric characteristics of the resulting coated wire electrode [21]. The potentiometric characteristics of the electrode are also influenced by the conditioning system, such as the duration of the conditioning, the concentration of conditioning solution, and the acidity of the solution [21, 22].

The conducting polymers, because of its ionic and its conductivity, have an ionic transducer ability, which is good for electrons in ionic sensor and biosensor electrodes. It is found that the conductivity and morphology of polypyrrole were also influenced by dopants trapped in the polypyrrole membrane matrix [23]. The electric conductivity of the membrane influences the rate of electron movement through conducting membrane. While the morphology of polypyrrole affects the ionic mobility of dopants and the physical stability of the membrane, a metal-wire electrode coated with polypyrrole membrane containing anionic surfactant dopants will shortly respond to the same anion in the analyte solution [24]. Nevertheless, the relationship between membrane electrical conductivity and the sensitivity of the electrodes' potential response has not been reported accurately.

During the measurement of anionic surfactant using ISE, a potential response resulting from the redox mechanism is developed between the indicator electrode with a reference electrode and equilibrium system at the interface of electrode and analyte solution. At those interfaces, an ionic exchange is developed between dopant anions trapped in the polymer membrane with the same anion of analyte surfactant. When the redox reaction produces a constant potential difference and the concentration of dopant anions in the polymer membrane is also constant, then, based on the Nernst equation, the measured cell potential will only be influenced by the concentration of surfactant anion in the analyte solution [24].

The aims of the research are to electrochemical synthesis and to directly coat polypyrrole membrane using cyclic voltammetry technique and then to study the potential of the polymer as a mediator membrane candidate for SDS surfactant potentiometric electrode sensor. Based on the results of the research, this paper reports the optimum parameters of cyclic voltammetry applied for synthesis and coating polypyrrole at the surface of the gold-wire electrode in the electrochemical cell containing a mixed solution of pyrrole,  $\text{NaClO}_4$  or SDS supporting electrolyte, and  $\text{DS}^-$  anions as dopant species. The membrane was coated at the gold-wire electrode surface during the pyrrole electropolymerization in those mixed solutions. The gold-wire electrode coated with the membrane is then be used to measure the potential response of  $\text{DS}^-$  anion in the SDS analyte solution.

## 2. Methodology

Electrochemical polymerization of pyrrole was performed in electrochemical cells using the cyclic voltammetry technique. All chemical materials and equipment used were available in Analytical Research Laboratory.

### 2.1. Materials

The primary materials used in this research were 98% pyrrole solution as a monomer material of synthesized polypyrrole, sodium dodecyl sulfate (SDS) as standard analyte solution, source of  $\text{DS}^-$  anion dopant, supporting electrolyte, and conditioning solution for polypyrrole coated gold-wire electrodes. Besides of SDS surfactant, this research also used  $\text{NaClO}_4$  solution as a supporting electrolyte during the electropolymerization process. All those materials were purchased from SIGMA. Electrode materials used in electropolymerization processes by cyclic voltammetry were gold (Au) wire as indicator electrode, platinum (Pt) wire as the auxiliary electrode, and silver-coated silver chloride ( $\text{Ag}/\text{AgCl}$ ) as the reference electrode.

### 2.2. Equipment

Some tools used to preparation of solution were 25-mL graduated cylinder, 25-mL graduated volumetric flask, 30-mL polyethylene bottle, and other standard glass equipment. Weighing of chemical materials was carried out using an electric weighing of the METER AE 200 model with an empty weight of 0.0000 g.

Electropolymerization and electrocoating of the gold-wire electrode were performed using a potentiostat *IdInstrument 400* model connected to a voltammetric cell. This cell was equipped with three electrodes: Ag|AgCl with a diameter of 0.5 mm and length of 10.0 cm as a reference electrode, platinum wire with a diameter of 0.2 mm and length of 5.0 cm as the auxiliary electrode, and gold wire with a diameter of 1.0 mm and length of 5.0 cm as indicator electrode. These electrodes were dipped in a voltammetric cell containing a mixture solution of polymerization and were connected to a potentiostat mounted on a computer recording. The obtained polypyrrole coated gold wire electrodes were then observed to reveal and further develop its capability as a DS<sup>-</sup> anion electrode sensor.

Potentiometric measurements were performed using polypyrrole coated gold wire electrodes as working electrodes and Hg|Hg<sub>2</sub>Cl<sub>2</sub> as a reference electrode. Both electrodes were connected to the pH/Voltmeter ORION 420A model and dipped in the 50-mL potentiometric cell containing a magnetic stirrer. The potential responses obtained from the measurements were recorded from the pH/Voltmeter.

### 2.3. Experiments

Laboratory experiments carried out in this research included electrochemical synthesis and electrodeposition of polypyrrole on the surface of the gold wire electrodes and observing the capability of the coated wire electrodes as sensor electrodes for analyte SDS surfactant.

#### 2.3.1. Electrosynthesis and electrocoating of polypyrrole

The coating of the electrode with polypyrrole was carried out in a continuous process of pyrrole electropolymerization on the surface of the gold-wire electrode using a cyclic voltammetric technique in an electrochemical cell equipped with three electrodes. In those processes, the gold-wire electrodes were placed as working electrodes. The gold-wire was rubbed by silica powder to clean its surface before dipped into a voltammetric cell. Two other electrodes were platinum wires as auxiliary electrodes and Ag/AgCl as reference electrodes. The process of electropolymerization was carried out in the 10-mL voltammetric cell containing a mixture of pyrrole, dopants, and supporting electrolytes. The cyclic voltammetry parameters observed were the potential range of scanning and scanning rate.

The cyclic voltammetry of pyrrole electropolymerization was performed by repeat potential scanning from negative to positive and from reverse direction of potential value for ten cycles with an electric current of 2 mA. These processes were performed in a voltammetric cell containing 0.01 M pyrrole, 0.01 M NaCl supporting electrolyte. The variation of potential range of scanning observed were: (1) -0.5–1.0 V, (2) -0.6–1.0 V, (3) -0.7–1.0 V, (4) -0.8–1.0 V, (5) -0.9–1.0 V, and (6) -0.9–1.1 V, with scanning rate of potential of 50, 80, and 100 mV/s, respectively. Electropolymerization was also performed using a mixed solution of 0.01 M pyrrole and 0.001 M SDS.

#### 2.3.2. Potential electrode measurements

Polypyrrole coated gold-wire electrodes produced from this experiment are now called Au-PPy-DS. Before and after use for measurements, the electrodes were soaked for a while in SDS solution to activate dopants trapped in the membrane, activate ionic equilibrium at the solution interface and membrane surface, and remove undesired site products electropolymerization reaction [21]. The electrodes were also soaked by tissue paper to dry and to clean the impurity.

Au-PPy-DS and saturated calomel (Hg|Hg<sub>2</sub>Cl<sub>2</sub>|3 M KCl) electrodes were then dipped in the analyte SDS solution to measure the potential response of the electrode toward DS<sup>-</sup> analyte in the concentration range of 10<sup>-9</sup>–10<sup>-2</sup> M. The constant potential response produced from these measurements were recorded and plotted to the negative logarithm of SDS concentration (pSDS) to determine calibration curves, the limit of detection, and sensitivity of electrode. The electrode detection limit was recorded from the lowest concentration value of the extrapolated calibration curve, while the electrode sensitivity was recorded from the slope value of the linear (calibration) curve by mV/decade unit.

## 3. Results and Discussion

### 3.1. Voltammetrically Electrocoating of Polypyrrole

It was observed that polypyrrole could be synthesized by the electrochemical method. Cyclic voltammetry is the most used technique applied in the characterization of conducting polymer such as polypyrrole. This technique is applied by scanning the potential in the forward and reverse directions during the electropolymerization oxidation-reduction process of aqueous pyrrole solution. This electropolymerization applies an electric current to force a redox reaction caused by diffusion current only [25]. To prevent the appearance of migration currents, a supporting electrolyte is added to the aqueous pyrrole solution, an electroactive solution having higher activity than analyte solution [25]. The addition of supporting electrolytes also aims to increase the solution electric conductivity. Electropolymerization by cyclic voltammetry is inaccurate in the absence of supporting electrolyte. To prevent convection currents, electropolymerization with this technique is also carried out in a non-stirred solution. The morphology of polymer membrane produced depends on electrolyte nature, scanning rate and potential of depositions, monomer concentration, and pH of solution [19].

Polypyrrole electrocoating on the surface of the gold-wire electrodes by cyclic voltammetry was carried out with variations in the potential range and the scanning rate. Pyrrole, C<sub>4</sub>H<sub>5</sub>N, is a water-soluble conjugated monomer and undergoes redox reactions under specific potential range and scanning rate. Potential scanning can be done repeatedly from negative to positive and vice versa. Under the negative to the positive direction running off the potential scanning, pyrrole monomers are oxidized to cationic radical monomer. Dimers are formed under reverse direction by the reduction reaction of the cation, and so on until

polymer formed under the direction of the cycle of performing potential scanning repeatedly. The general mechanism for the propagation of electrochemically polymer chain formation is described by the sequential reaction, as shown in Figure 1 [26].

The resulting polypyrrole is coated directly on the surface of the gold-wire electrodes with a certain thickness. A typical cyclic voltammogram recorded from a polypyrrole formation depended on the solvent, the supporting electrolyte used, and cyclic voltammetry parameters applied [27, 28].

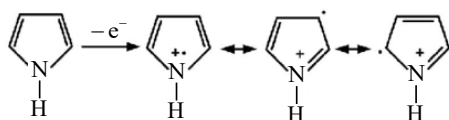
Pyrrole electropolymerization is processed and developed under a complex reaction mechanism. Some problems of the polymer, such as the formation process, the formation mechanism, and the charge naturalization, structure, properties, and synthesis conditions used, are debatable today [27]. The complete mechanism of polypyrrole formation is obtained when there are no redox reactions from other species during pyrrole electropolymerization. The pyrrole electropolymerization process must be carried out under a specific potential range where the typical potential peak

and the current peak will be read and separated from those of other species. This is why the researcher always performs electropolymerization processes in various potential ranges to obtain valid data.

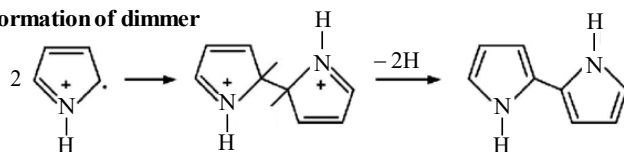
In this study, cyclic voltammograms generated from the pyrrole electropolymerization process are presented in various potential scanning ranges. It appears that these parameters affect the oxidation and reduction of the peak polymer current (Figure 2).

Based on the anodic and cathodic peak currents shown by those voltammograms (Figure 3), it is known that equilibrium redox reaction of the polymerization is accurate when potential scanning is run under a potential range of -0.9–1.0 V. Under this potential range, the resulting polypyrrole membrane has possible better electrical conductivity than that of under other potential ranges. The cyclic voltammogram is shown in Figure 2 also describes that the overoxidation possibility is inaccurate when potential scanning of pyrrole electropolymerization is run under the potential range of -0.9–1.0 V.

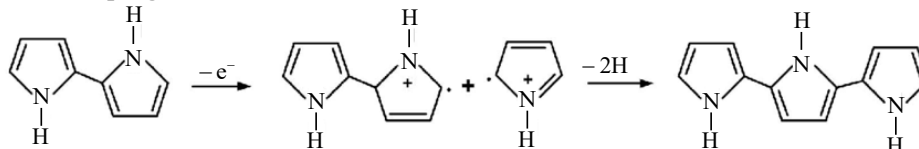
**Pyrrole oxidation**



**Formation of dimer**



**Oxidation, coupling, and rearomatization**



**Chain propagation**

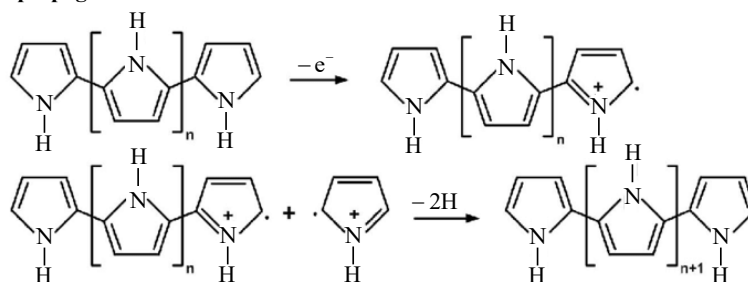
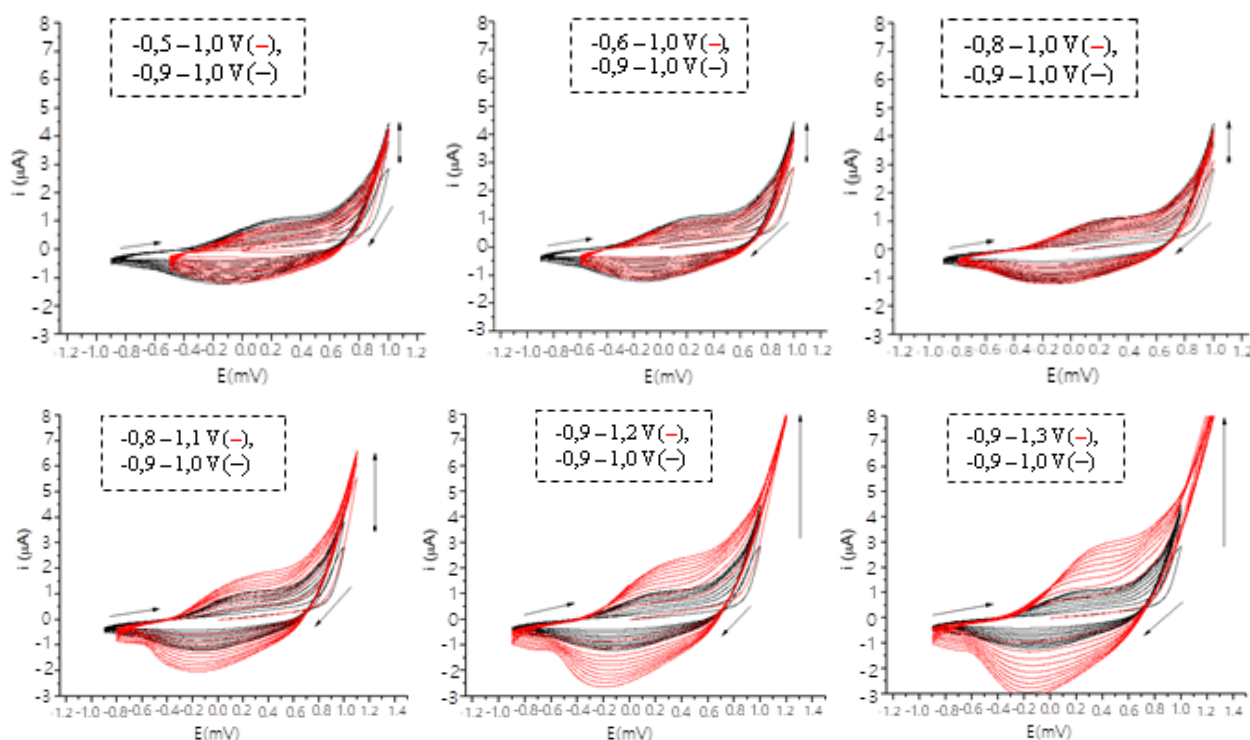
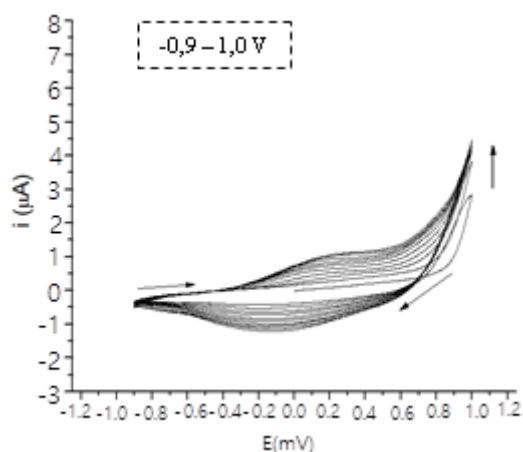


Figure 1. The general mechanism for the propagation of electrochemically polypyrrole formation.





**Figure 2.** Cyclic voltammograms of 0.01 M pyrrole electropolymerization in aqueous solution containing 0.01 M NaClO<sub>4</sub>. Potential scanning runs on various potential ranges with an electric current of 2 mA and a scanning rate of 100 mV/s for ten cycles. The direction of the right and down arrows indicate the scanning direction, while the direction of the up arrow indicates the current shifts from the first running of potential scanning.

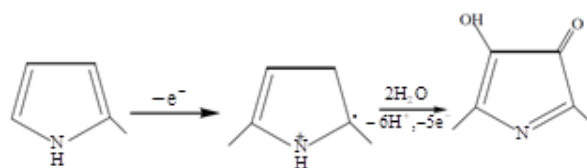


**Figure 3.** Cyclic voltammograms of electropolymerization of 0.01 M pyrrole in an aqueous solution containing 0.01 M NaClO<sub>4</sub>. The potential scanning is carried out under a potential range of -0.9–1.0 V, an electric current of 2 mA, and a scanning rate of 100 mV/s for ten cycles. The right and down directions of the arrow show a scanning direction, while the direction of the up arrow indicates the current shifts from the first running of potential scanning.

The potential increase from -0.9 V to -0.5 V is not influenced by the high of anodic and cathodic currents but is influenced to reduce the range of potential scanning needed. With the application, the scanning rate is constant, decreasing the range of potential scanning that is influenced by the electropolymerization time, and then influencing the perfection of the polymer formed. Conversely, an increase in the reverse directions of

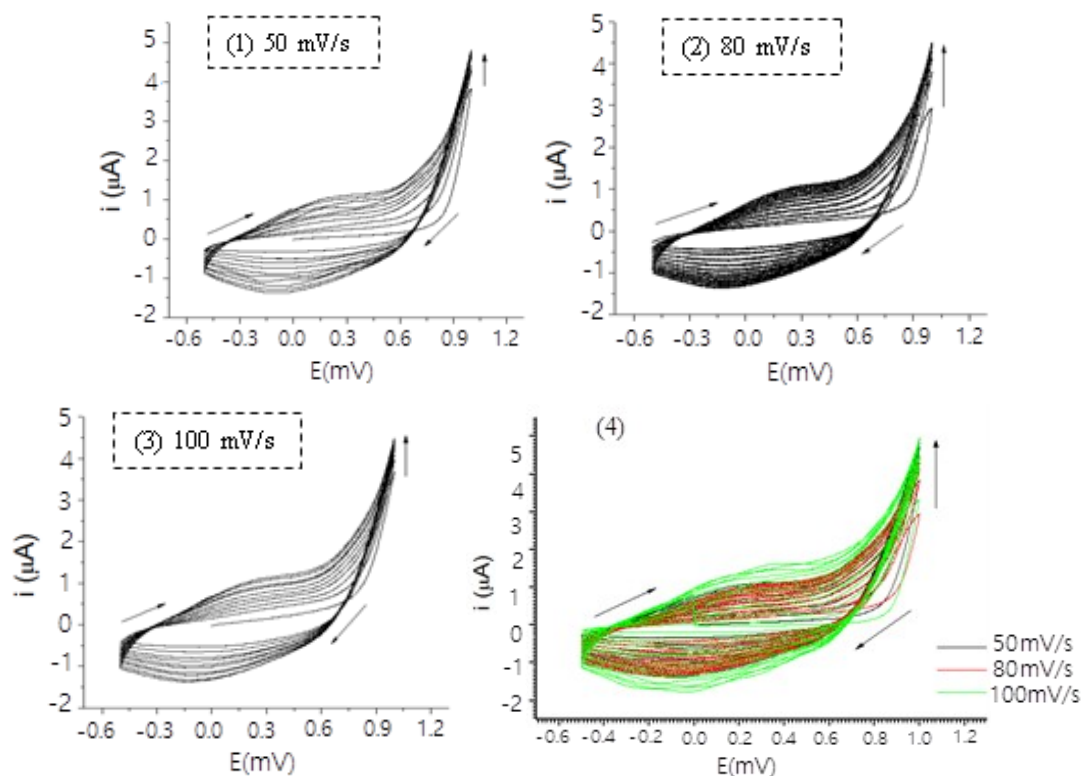
potential scanning of 0.1 V and more causes a shift and an increase in the anodic and cathodic peak currents, so the potential scanning under a range of -0.8–1.1 V, -0.9–1.2 V, dan -0.9–1.3 V produced new cathodic peak currents and imperfect polypyrrole membrane structure. The new cathodic peaks current indicates that other reductions from another species are occurring.

Overoxidation in pyrrole electropolymerization tends to be accurate by an irreversible redox reaction, as shown in Figure 4 [29]. The conjugation system of polypyrrole is disrupted by a decrease in conductivity and rechargeability loss of the polymer.



**Figure 4.** Overoxidation mechanism of polypyrrole

The potential of over reduction and overoxidation does not appear at potential scanning run above -0.5 V (Figure 1). This fact is emphasized by the previous report showing that the potential of over reduction and overoxidation appears on potential scans that run below -0.5 V only [30]. This phenomenon occurs only when pyrrole electropolymerization is carried out in acidic or basic solution due to the water oxidation reaction [28]. Under the acidic and basic conditions, water molecules are oxidized at -1.068 V and -0.191 V, respectively, concerning Ag/AgCl reference electrode [31].



**Figure 5.** Cyclic voltammograms of electropolymerization of 0.01 M pyrrole in an aqueous solution containing 0.01 M NaClO<sub>4</sub>. The potential scanning is run under a potential range of -0.9–1.0 V, an electric current of 2 mA, and a scanning rate of 50 mV/s (1), 80 mV/s (2), and 100 mV/s for ten cycles. Right and down directions of arrow show a scanning direction, while up the arrow direction showed currents shift from the first running of potential scanning.

As reported by previous studies [27, 32, 33], these observations reveal the optimal scanning potential range for the pyrrole electropolymerization process in aqueous solution by cyclic voltammetry is -0.9–1.0 V. In this potential range, overoxidation and overreduction of pyrrole electropolymerization did not occur [29]. Pyrrole electropolymerization by scanning rate of 50, 80, and 100 mV/s obtained cyclic voltammograms are shown in Figure 5. All cyclic voltammograms exhibit that overoxidation and overreduction are not involved in the electropolymerization.

Pyrrole electropolymerization by scanning rate of 50 mV/s and 80 mV/s produces similar cyclic voltammograms, while the electropolymerization by scanning rate of 100 mV/s produces higher oxidation and reduction peak currents than its monomer and the polymer (Table 1).

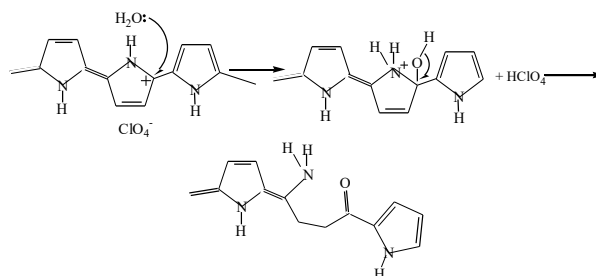
**Table 1.** Typical parameters of pyrrole electropolymerization based on scanning rate

Scanning Rate (mV/s)	Peak Current ( <i>i</i> )		Peak Potential ( <i>E</i> )	
	Anodic, <i>i</i> <sub>p</sub> <sup>a</sup> (µA)	cathodic, <i>i</i> <sub>p</sub> <sup>c</sup> (µA)	Anodic, <i>E</i> <sub>p</sub> <sup>a</sup> (V)	cathodic, <i>E</i> <sub>p</sub> <sup>c</sup> (V)
50	1.1	-1.4	0.24	-0.2
80	1.1	-1.4	0.24	-0.2
100	1.6	-1.8	0.36	-0.5

Pyrrole electropolymerization by lower scanning rate than 100 mV/s proceeds slowly so that the electropolymerization needs a more extended time. Under the slow process of electropolymerization, a part of

previously formed cationic radicals reacts with water solvent before reacting with monomer molecules so that the existence of reaction phenomena shown in Figure 4 is established.

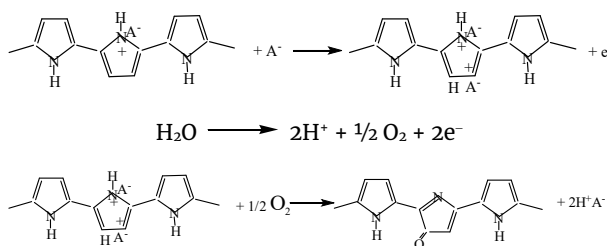
On the other hand, pyrrole electropolymerization with a scanning rate of more than 100 mV/s produces too many cationic radicals so that the irreversible formation reaction of the polymer is accurate and imperfect polymers are formed. There is not enough time for cationic radicals to develop a chain reaction to form a perfect polymer under a too rapid scanning rate of electropolymerization processes. It is a consequence of the site reaction of cationic radicals with water molecules, as shown in Figure 6 [10].



**Figure 6.** The secondary reaction of pyrrole electropolymerization in an aqueous solution containing ClO<sub>4</sub><sup>-</sup> supporting electrolyte.

The reaction of polypyrrole cations with water molecules, as shown above, is accurate under the potential range where those radicals are oxidized more readily than their monomers. This reaction causes a

higher reduction peak current of the polymer than the oxidation peak current. Running the potential by too high scanning rate during pyrrole electropolymerization also causes an over dimerization reaction, followed by releasing H<sup>+</sup> ions into the solution so that the solution's acidity increases. Under acidic solution, water molecules will be oxidized to form oxygen molecules so that the second reaction is accurate, as shown in Figure 7 [28].

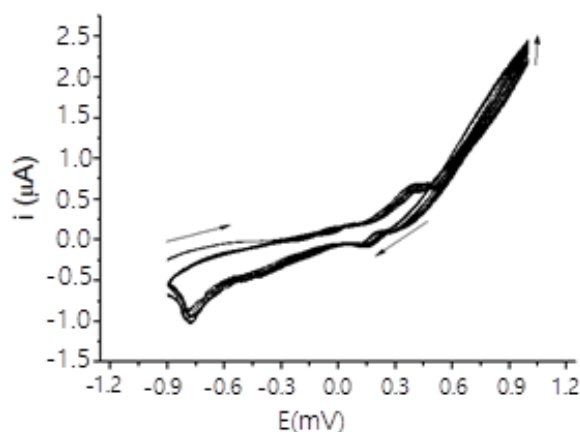


**Figure 7.** The secondary reaction of polymerization of pyrrole in the water containing A<sup>-</sup> supporting electrolyte under acidic condition.

Previous research has shown that the optimum scanning rate of pyrrole electropolymerization using cyclic voltammetry technique is 100 mV/s. The pyrrole electropolymerization process under a scanning rate of more than 100 mV/s will produce an imperfect polymer [34].

### 3.2. Pyrrole electropolymerization in the SDS solution

The cyclic voltammogram of pyrrole electropolymerization in the aqueous SDS solution is shown in Figure 8. One oxidation peak current appears on the voltammogram at 0.4 V, and three reduction peak currents appear at 0.7 V, 0.1 V, and 0.3 V.



**Figure 8.** Cyclic voltammogram of electropolymerization of 0.01 M pyrrole in an aqueous solution containing 0.01 M SDS. The potential scanning is run under a potential range of -0.9–1.0 V, an electric current of 2 mA, and a scanning rate of 100 mV/s for five cycles. Right and down directions of arrow show a scanning direction, while up the arrow direction showed currents shift from the first running of potential scanning.

The occurrence of the electropolymerization proves the role of SDS as a supporting electrolyte. Electropolymerization of conducting polymer would not be conducted in the absence of supporting electrolyte [19, 35]. The addition of supporting electrolytes is primarily

intended to present the current of migration, which inhibit the required diffusion currents [23]. The cyclic voltammogram also shows that the SDS surfactant increases the solution conductivity.

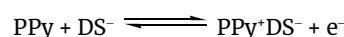
Pyrrole electropolymerization involves the formation mechanism of polypyrrole cation (PPy<sup>+</sup>). The existence of DS<sup>-</sup> anion from SDS surfactant in the aqueous pyrrole solution during electropolymerization processes is influenced by the polypyrrole formation reaction by three possible phenomena: (1) Electrostatic interaction between DS<sup>-</sup> anions and polypyrrole cations; (2) Trapping the hydrophobic chain of DS<sup>-</sup> anions in the matrix of the polymer formed (3) Micelle formation of surfactant influences the distribution of DS<sup>-</sup> anions in the micelle and aqueous phases.

The different roles of SDS and NaClO<sub>4</sub> as supporting electrolytes are related to their molecular structures. The SDS molecules have a long chain hydrophobic tail that causes mobility in the observed solution to be too slow than NaClO<sub>4</sub>. Cyclic voltammograms of pyrrole electropolymerization in the existence of those supporting electrolytes describe the differences (Figures 3 and 8).

### 3.3. Potential response of electrode to DS<sup>-</sup> anions

Polypyrrole coated gold-wire electrode obtained from the electrochemical process by cyclic voltammetry technique is then observed its possible compatibility as SDS surfactant sensor electrode (abbreviated as Au-PPy-DS). By this observation, the potential of polypyrrole membranes as a mediator membrane candidate for the construction of the SDS surfactant sensor electrode is proven and can be intensively developed and further observed.

The electrode potential response can be explained based on the interface equilibrium exchange of DS<sup>-</sup> anions developed during SDS measurements [35, 36]. When the electrode is dipped in the aqueous SDS solution, the shift of the DS<sup>-</sup> anions and the ion concentration gradient around the electrode surface causes the shift of DS<sup>-</sup> anions in the polypyrrole membrane to reach equilibrium between the membrane interface and aqueous analyte solution. This equilibrium is developed by the chemical equation as follow:



The potential response (E) of the electrodes resulting from the above reaction is derived by following Nernst equation:

$$E = E^0 + (RT/nF) \ln \frac{a_o}{a_r \cdot a_{\text{DS}}}$$

where *a<sub>o</sub>* and *a<sub>r</sub>* are oxidized (PPy<sup>+</sup>) activities and reduced (PPy) forms of polypyrrole membrane, respectively, while *a<sub>DS</sub>* are the DS<sup>-</sup> anion activity in the aqueous solution. Because the membrane doping level is constant, then the equation above can be simply written as:

$$E = E^0 - (RT/nF) \ln a_{\text{DS}}$$

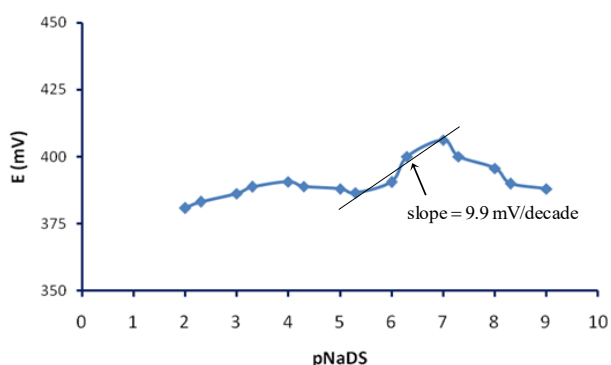
$$= E^0 - (2,303 RT/nF) \log a_{\text{DS}}$$

The last equation informs that the electrode's potential is straightly proportional to the activity or concentration of  $\text{DS}^-$  analyte, and therefore, the electrode is applicable to determine SDS surfactant potentiometrically. The  $2,303 RT/nF$  value is referred to as the sensitivity of electrode in the unit of mV/decade.

As shown in Figure 9, the Au-PPy-DS electrode obtained in this observation is proved to be able to respond to the  $\text{DS}^-$  anions from analyte solution in the concentration range of  $10^{-7}$ – $10^{-5}$  M, with the sensitivity of electrode of 9.9 mV/decade and limit of detection of  $10^{-7}$  M.

The electrode capability to respond to  $\text{DS}^-$  anions describes that a small part of the SDS molecule is trapped in the matrix of polypyrrole membrane during pyrrole electropolymerization. These  $\text{DS}^-$  anions then acts as a dopant ionophore in the potentiometric measurement of the  $\text{DS}^-$  analyte by Au-PPy-DS.

The electrode sensitivity value is still too low than the Nerstian value (59 mV/decade). However, the electrodes' ability to detect  $\text{DS}^-$  anion analytes provide a good indication that the polypyrrole membrane is coated on the surface of the gold wire electrodes produced from this experiment, enabling the  $\text{DS}^-$ -anion exchange mechanism. So, this type of electrode can be further designed to be an elective-selective ion (ISE) for the determination of SDS surfactants with innovative research parameters.



**Figure 9.** Potential response of the Au-PPy-DS electrode.

Preparation of the electrode was performed by cyclic voltammetry technique under a potential range of running of  $-0.9$ – $1.0$  V, the scanning rate of  $100$  mV/s, and electric current of  $2$  mA for  $60$  cycles.

Electropolymerization was performed in the electrochemical cell containing the mixture solution of  $0.05$  M pyrrole and  $0.001$  M SDS. The sensitivity of the electrode to  $\text{DS}^-$  anion was  $9.9$  mV/decade.

The sensitivity value is not the only parameter of electrode capability, but it is the first substantial information for evaluating the electrode's potential behavioral response. The electrode's sensitivity is still far from the Nerstian value for a single-charged analyte ( $59$  mV/decade). Nevertheless, as a preliminary study, this value is a good indication for the observed electrode to be developed in future studies.

To increase electrodes' sensitivity, studies to determine the optimal solution composition of the

electropolymerization, such as pyrrole concentration, type and concentration of supporting electrolyte, and the content of  $\text{DS}^-$  ionophore are needed. The study of cyclic voltammetry parameters is developed to obtain the optimal thickness of the membrane if the polymer membrane thickness also influences the electrode's sensitivity.

While the main potentiometric parameters that will be further observed are the Nerstian sensitivity of electrode, the range of measurement concentrations or calibration curve, and the limit of detection, those parameters are determined by plotting the potential response of the electrode as a function of the concentration of analyte SDS solution. The sensitivity of the electrode is determined from the slope of the calibration curve, while the limit of detection is determined from the lowest value of  $\text{DS}^-$  concentration in the extrapolated line of the calibration curve.

#### 4. Conclusion

Electrocoating polypyrrole at the surface of the gold-wire electrode can be conducted directly by cyclic voltammetry technique in the electrochemical cell containing pyrrole with the existence of supporting electrolyte species. The chemical and physical characteristics of the polypyrrole membrane depend on parameters of cyclic voltammetry applied, such as the potential range of scanning, scanning rate, and the existence of supporting electrolytes.  $\text{DS}^-$  anion dopants are trapped directly in the polypyrrole membrane matrix during the electropolymerization process in the electrochemical cell containing supporting electrolyte of inorganic salts. The  $\text{DS}^-$  dopant trapped in the polymer roles as ionophore to recognize  $\text{DS}^-$  anions in the SDS surfactant of analyte solution.  $\text{DS}^-$  anion itself also acts as a supporting electrolyte in electrochemical cells without supporting electrolyte of inorganic salts. Polypyrrole coated on the surface of the gold-wire electrodes is proved applicable as a potential mediator membrane for the electric conductor and ion exchanger during the measurement of  $\text{DS}^-$  anions in an aqueous sample solution.

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