

Development of Solid State Reference Electrode Based on Polypyrrole (PPy) and Screen-Printed Electrode (SPE)

SAGIR ALVA^{1*}, MAS'UD ASADULLAH¹, VIVI FRILIANDITA², DENI SHIDQI KHAERUDINI^{1,3}

¹Postgraduate of Mechanical Engineering Department, Faculty of Engineering, Universitas Mercu Buana, West Jakarta, Jakarta, 11650, Indonesia

²Mechanical Engineering Department, Faculty of Engineering, Universitas Mercu Buana Mercu Buana, West Jakarta, Jakarta, 11650, Indonesia

³Research Center for Advanced Materials, National Research and Innovation Agency (BRIN) Kawasan Puspiptek, Serpong, South Tangerang 15314, Indonesia

*Corresponding Author: sagir.alva@mercubuana.ac.id; Phone Number: +6285779381297

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Abstract. In this study, a Polypyrrole doped KCl/KCl saturated (PPy-Cl/KCl) reference electrode had been successfully developed. In this development process, the PPy-Cl/KCl reference electrode that had been provided consisted of two stages of refinement, specifically the PPy-Cl/KCl 1 reference electrode which became the PPy-Cl/KCl 2 reference electrode. Furthermore, the PPy-Cl/KCl 2 SRE was made into 3 types with cycle variations of 10, 15, and 20 cycles and the mV response value test and Scanning Electron Microscopy (SEM) test were carried out. Regarding the variation results, PPy-Cl/KCl 2 SRE was obtained with 15 cycles as the best PPy-Cl/KCl 2 reference electrode with ΔmV value of 3.43 mV. Subsequently, the PPy-Cl/KCl 2 SRE with 15 cycles was involved in the characterization test using cyclic voltammetry (CV) testing, response testing vs Cl sensors and drift testing. In the CV testing, the PPy-Cl/KCl 2 SRE with 15 cycles indicated a voltammogram graphic pattern similar to the Ag/AgCl reference electrode as a commercial reference electrode. Moreover, in the response testing vs the Cl sensor, the PPy-Cl/KCl 2 SRE with 15 cycles provided a Nernstian number value of -54.5 mV/s with a testing range of $0.1-10^{-4}$ M, and in the PPy-Cl/SRE drift testing, KCl 2 with 15 cycles indicated fairly good stability, particularly with a drift value of 1 mV/minute which was achieved after the conditioning process after 3.5 minutes.

Keywords: Polypyrrole, solid-state, reference electrode, screen-printed electrode, SPE

INTRODUCTION

The reference electrode is commonly defined as one of the most potential components in electrochemical measurements. The reference electrode is considered capable of providing influence on the measurement

results and accuracy. Moreover, a good reference electrode is able to provide a stable potential and is not prone to changes in the environment or sample.

In general, reference electrodes may have a rod-like shape and tend to be used independently of the working electrode or sensor. The shape is likely not appropriate to be utilized in in-situ measurements of spaciousness. Spaciousness is usually measured using a portable device. As an alternative, it is highly required to develop a reference electrode which has a small size and can be integrated with the working electrode in a single body. Consequently, in-situ measurements can be carried out more practically and easily.

Several previous researchers have widely provided efforts to develop small-sized reference electrodes. The type of solid was generally used by previous researchers which are then often referred to as a solid reference electrode (SRE). The solids used are generally in the form of membranes doped with electrolytes or with lipophilic salts.

There have been several studies that previously focused on solid reference electrodes specifically by Francesca Criscuolo by means of 4 different membrane models on solid reference including PVB, Agar, PVC and IL(Ionic-Liquid-doped)-PVC. This study indicated that PVB, PVC, and IL-PVC membranes were capable of providing good stability and reproducibility with subtle differences depending on the application and on the working pH of the solution. Moreover, agar was not found to provide any significant improvement [1].

Another study had been successfully carried out by Dewi using Cu/CuSO₄ as a membrane for solid reference electrode. This study compared 2 forms through the use of cotton and without using cotton. The results of this study indicated that Cu/CuSO₄ membranes were more likely to have better results by using cotton [2].

The reference electrodes studied previously were generally metal based and easily oxidized, which could subsequently result in unstable reference electrodes. Consequently, it is urgently needed to have another non-metal based alternative, specifically by using polypyrrole. Previous studies had mostly used sodium methanol sulfonate and CA membranes.

Polypyrrole is classified as a conductive polymer. Conductive polymers are defined as good conductors of electricity. Currently, the application of conductive polymers has been frequently examined by researchers, particularly in the fields of sensors, biosensors, ion-selective membranes, transistors, capacitors and batteries. Furthermore, the conductive polymer may also be used for the transport of bioactive molecules due to its redox properties which are capable of controlling the transport of ions across the polymer membrane [3].

In this study, a reference electrode was made by utilizing polypyrrole on a screen printed electrode (SPE) for the electrochemical measurement method. In the first stage, an initial design was made for the PPy-Cl/KCl SRE, then several variations of the voltametric cycle were carried out to obtain good results. Moreover, Cyclic Voltammetry (CV) testing, testing with the Cl sensor, and drift testing were also successfully carried out at the next stage.

METHODOLOGY

Instrumentations

Some of the equipment that was successfully used in this study consisted of the Corrtest CS350 electrochemical workstation from Corrtest Wuhan Instrument Corp., Ltd., Scanning Electron Microscopy (SEM), Orion® 900200 double-junction Ag/AgCl reference electrode from Thermo Fisher, pencil graphite electrode (PGE) type 2B from Faber Castell, and carbon electrode with SPE type from Sprint Print Bhd Malaysia.

Materials

In this study, several materials were used including pyrrole monomer from sigma-aldrich, epoxy resin and hardener from Dextone, KCl salt from Cica-reagent, cellulose acetate (CA) from Sigma-Aldrich, Gelatin Powder from lieliakiau (shopee), facial cotton from Selection, PTFE Teflon Tube from rajacellbekasi (shopee) and acetone from Merck.

Experimentals

This study was successfully carried out through several stages. In the first stage, an initial design of the PPy-Cl/KCl 1 SRE and PPy-Cl/KCl 2 SRE was made. The second stage was to perform a cycle voltametric variation to obtain good results by referring to the ΔmV KCl response value. After getting the best results, then a Cyclic Voltammetry (CV) test was carried out to be compared with a commercial reference electrode, and a Cl sensor was tested to determine the slope of the reference electrode made, and finally a drift test was carried out to examine the stability of the reference electrode made.

Carbon screen printed electrode (SPE) was prepared in the process of making the PPy-Cl/KCl 1 SRE reference design. Then, Cyclic Voltametric (CV) process test was carried out on 0.1M KCl solution to determine the reaction before being coated with Pyrol. After successfully carrying out the CV test with 0.1 M KCl solution, the pyrol was coated using the CV test on the pyrol solution with 10 cycles. After that, the CV test was also carried out with 0.1 KCl solution.

After the pyrol had been coated, the electrodes were then wiped with a tissue. Subsequently, the surface of the pyrol electrode was first coated with 20 mL of 5% Acetone and Cellulose Acetate (CA) solution and then evenly allowed to stand for about 1 hour for the drying process. After that, the surface was coated using Jelly with a composition of 10 ml, 1 g KCl, and 5 g gelatin. After that, it was evenly coated with 20 mL of acetone and 5% CA solution and allowed to dry. Furthermore, this electrode was defined as PPy-Cl/KCl 1 SRE as shown in Figure 1 below.

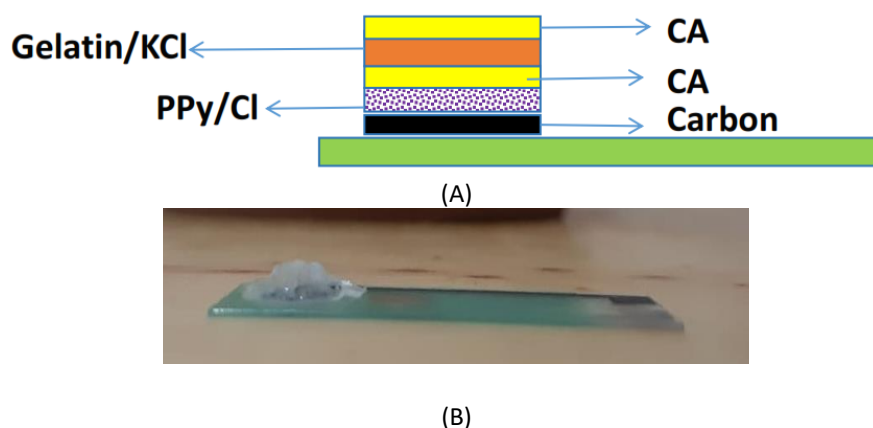


Figure 1. (A) Structure of PPy-Cl/KCl 1 SRE layer, B. PPy-Cl/KCl 1 SRE results

In the next step, PPy-Cl/KCl 2 SRE was made by giving 3 new parts. First, by adding a PTFE pipe as a wall and epoxy glue as an adhesive which aimed to allow the sample solution to enter through the top. The two layers of 20 mL of acetone and 5% CA solution were then replaced using cotton that had been soaked in acetone and 5% CA solution which aimed to improve adhesion. Finally, KCl salt was added between the cotton layer and the Jelly layer to increase the saturated KCl concentration at the electrode, as shown in Figure 2 below.

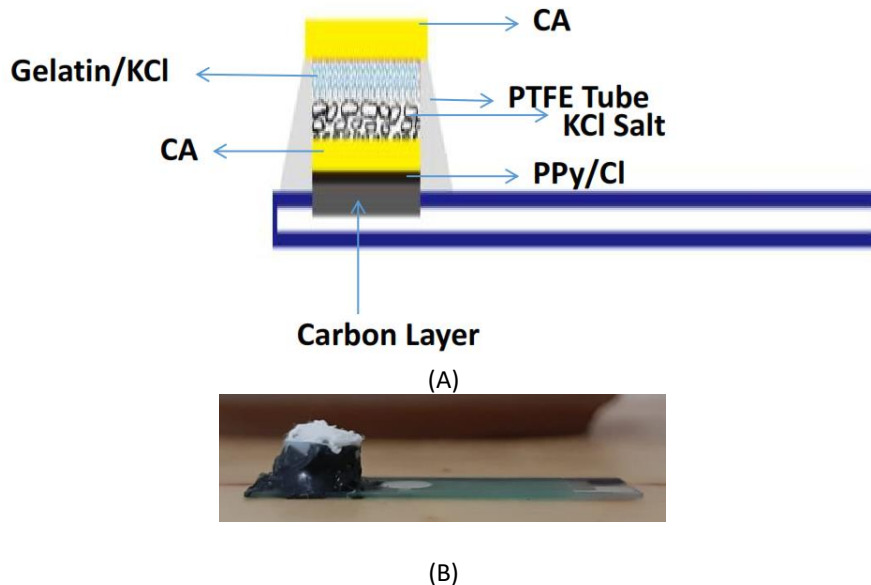


Figure 2. (A) Structure of PPy-Cl/KCl 2 SRE layer, (B). PPy-Cl/KCl 2 SRE results.

After PPy-Cl/KCl 2 SRE was successfully prepared, both designs were tested in KCl solution which had been immersed for 1 hour. The results of the immersion indicated that PPy-Cl/KCl 1 SRE was damaged by the release of the layer from the SPE, as shown in Figure 3. Therefore, this study was continued by using PPy-Cl/KCl 2 SRE.



Figure 3. SRE1 after soaking in 1 hour.

Figure 3. shows the part of the membrane that was lifted after the immersion. This was caused by the emergence of a reaction and the entry of the sample into the membrane. Therefore, PPy-Cl/KCl 2 SRE was chosen to be included in this study. Furthermore, the ΔmV KCl response test was successfully carried out, and PPy-Cl/KCl 2 SRE with the smallest ΔmV value would be included in the Cyclic Voltammetry (CV) testing, the testing with the Cl sensor, and the drift testing and dextone glue.

RESULTS AND DISCUSSION

Reference Electrode Design

In the early stages of this study, a PPy-Cl transducer had been prepared, where PPy-Cl was coated on the carbon surface of the SPE. To ensure the good quality of the carbon, then a test was carried out using the Cyclic Voltametric (CV) technique with 0.1 M KCl solution and the results were successfully obtained as shown in Figure 4 below:

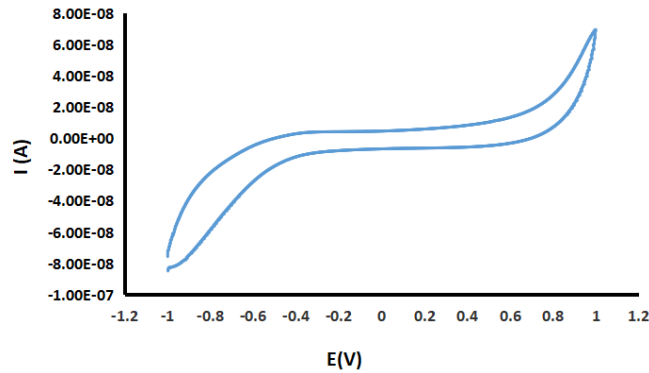


Figure 4. Cyclicvoltamogram (CV) of screen printed carbon electrode

Regarding to figure 4, it can be seen the character of the carbon electrode. One of the characters indicated by the carbon electrode is inert, inert has a non-chemical meaning of being unable to move or resist movement. it is capable of leading to the peak of oxidation or reduction does not appear. This result is in line with previous study [4].

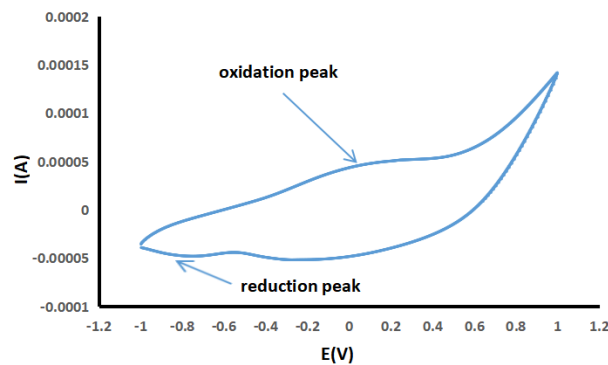


Figure 5. Cyclicvoltamogram of PPy/Cl on SPE

Figure 5 shows the results of the CV test after PPy-Cl coating was applied to the Ag surface. Subsequently, the CV test was repeated to ensure that the SPE carbon had been coated with PPy. This was urgently conducted because the colors before being coated with PPy-Cl and after being coated with PPy-Cl were almost the same, making it difficult to distinguish visually. In addition, Figure 5 shows the oxidation peak at 0.2 V. This indicates that the PPy-Cl layer had been successfully formed on the carbon surface. Regarding to theory, changes in the structure on the surface of the electrodes may change the cycle image of the resulting voltammogram.

ΔmV KCl Testing

A reference electrode has a stable potential value which cannot be affected by any changes in the sample environment such as sample potential concentration [5,6]. The stability of a reference electrode is highly correlated with the use of electrolyte salts in large concentrations. In Ag/AgCl reference electrodes, the electrolyte commonly used is salt. Having regard to the concept of Le Chartlier's principle of equilibrium, the high concentration of the electrolyte used may result in the equilibrium moving slowly from the reference electrode towards the sample in order to reach a new equilibrium point, where the concentration of the sample is usually lower. This may affect the sample to give almost no change in the potential at the reference electrode surface [6].

Referring to that matter, it may be stated that this ΔmV Cl ion test is considered crucial and highly required to be carried out. The three types of PPy-Cl/KCl 2 SREs that had been provided previously were then tested using various concentrations of KCl solution with a range between $0.1 - 10^{-4}$ M. In this test, the PPy-Cl/KCl 2 SRE would be paired with a commercial double-junction Ag/AgCl reference electrode, where the PPy-Cl/KCl 2 SRE would be functioned as a working electrode. Subsequently, it was connected to the electrochemical workstation and the mV value

generated from each test with KCl solution would be then recorded. The results of this ΔmV test can be seen in table 1 and figure 6 below.

Table 1. ΔmV Values of PPy-Cl/KCl 2 SRE with 10, 15, and 20 Cycles in variations in the concentration of KCl solutions ($0.1 \text{ M} - 10^{-4} \text{ M}$).

Log[KCl]	10 Cycle (mV)	15 Cycle (mV)	20 Cycle (mV)
-1	-253.42	-228.60	-223.00
-2	-253.30	-229.00	-220.00
-3	-232.36	-232.00	-217.00
-4	-227.58	-230.10	-223.00
ΔmV_{KCl}	25.84	3.43	5.83

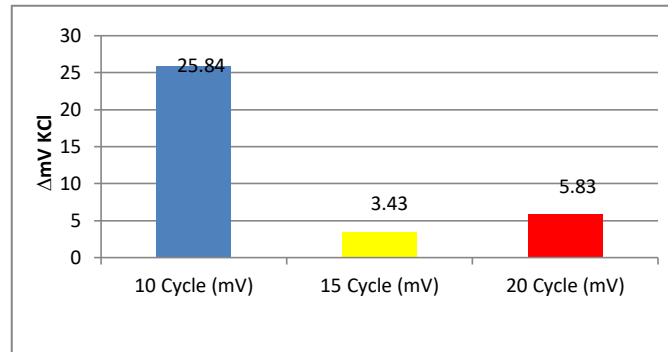


Figure 6. Value of mV KCl of PPy-Cl/KCl SRE with 10, 15, and 20 Cycles in KCl concentration variations of $0.1 - 10^{-4} \text{ M}$.

From table 1 and figure 6, it was found that PPy-Cl/KCl 2 SRE with 15 Cycle had the lowest ΔmV_{KCl} which was amounted to 3.43 mV. This result indicates that PPy-Cl/KCl 2 SRE with 15 Cycle provided characteristics as the reference electrode. Although the concentration of KCl had changed, the potential value generated by PPy-Cl/KCl 2 SRE with 15 Cycle was considered fairly stable. This is in contrast to PPy-Cl/KCl 2 SRE with 10 Cycle which produced $\Delta mV_{KCl} > 12 \text{ mV}$ of 25.84 mV. According to the reference electrode standard, the resulting value should not exceed 12 mV for the ΔmV test in the variation of the sample concentration [5]. Moreover, PPy-Cl/KCl 2 SRE with 20 Cycle was found between the two. Consequently, PPy-Cl/KCl 2 SRE with 15 Cycle was considered the most optimum and would be used for further testing.

The high value of ΔmV of PPy-Cl/KCl SRE was always influenced by the difference in the number of cycles. The difference in the number of cycles affected the slope and thickness of the PPy-Cl layer. The smaller the slope value and the thicker layer would be capable of affecting the sensitivity in detecting pH. This was highly needed to stabilize the resistance. This data can be seen in table 2 and 3.

Table 2. Comparison of the PPy-Cl slope on the electrode surface with variations in the number of cycles tested in pH solution (4,7 and 10).

Cycles	Slope (mV/dec)	R^2
10	52.61	0.9950
15	46.56	0.9940
20	43.02	0.989

Regarding to the thickness of PPy-Cl, SEM testing was carried out. In this study, SEM testing was used to evaluate the thickness of the PPy-Cl layer formed from cyclic differences in the manufacturing process. Prior to SEM testing, the carbon electrode was initially cut to determine the side of the electrode, as shown in Figure 7.

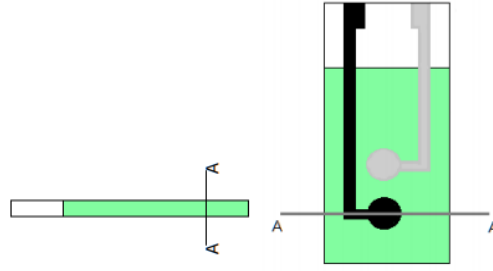


Figure 7. The shape of the electrode cut

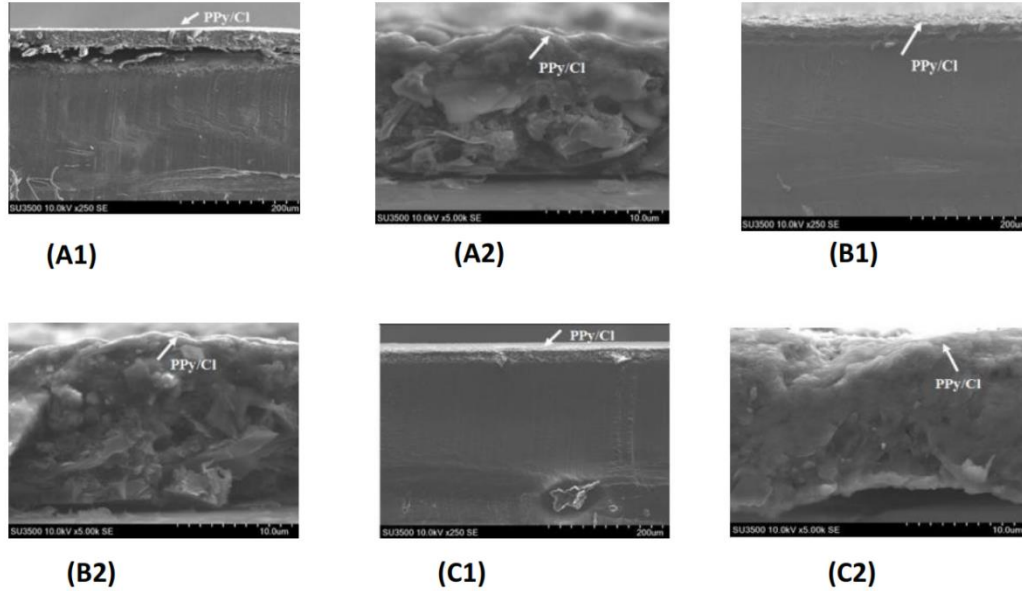


Figure 8. Results of the PPy-Cl reference electrode SEM

Figure 8 shows the results of the SEM images displayed at magnifications of 250 times (A1, B1, C1) and 5000 times (A2, B2, C2) with 10.0 kV illumination and inelastic reflection of secondary electrons (SE). Figure A1 – A2 shows PPy-Cl with 10 cycles, Figure B1 – B2 shows PPy-Cl with 15 cycles, and Figure C1 – C2 indicates PPy-Cl with 20 cycles. In the SEM test, the conductive layer showed a lighter color. The PPy/Cl layer formed is as shown by the arrow above. From Figure 8, it can also be seen the difference in the thickness of the PPy-Cl layer that was successfully formed. It is indicated that the cyclic with a higher amount produces a thicker PPy-Cl layer than the cyclic with a lower amount. Furthermore, the sample layer should be conductive to be capable of reflecting the electron beam and flowing it to ground, this should be conducted if observations were made by using SEM [7]. Referring to the figure, the PPy-Cl layer on the carbon surface had successfully appeared. This indicates that the PPy-Cl layer had been well formed and evenly distributed on the surface of the carbon electrode and also provided a conductive nature so that it could reflect the electron beam. The data related to the results of the PPy-Cl thickness measurements that had been formed are shown in Table 3 below.

Table 3 Measurement of PPy-Cl Thickness

Cycle	PPy-Cl Thickness (μm)
10	7.33 ± 0.08
15	12.00 ± 0.05
20	12.67 ± 0.06

Cyclic Voltammetry (CV) Testing

The CV test is referred to as a type of test used in electrochemistry. This test is able to describe a reduction and oxidation (redox) reaction mechanism from the surface of a test material. CV testing can be carried out by involving three electrodes, which include working electrodes, reference electrodes and auxiliary electrodes or known as counter electrodes [8]. This was intended to evaluate the performance of the PPy-Cl/KCl 2 SRE developed, whether it had the same capability as a commercial reference electrode. In this test, the prepared PPy-Cl/KCl 2 SRE would be paired with a carbon electrode of the SPE type which functioned as the working electrode and EGP as the auxiliary electrode. The three electrodes would be connected to an electrochemical workstation and immersed in a 0.1 M KCl solution as a test solution. The CV testing process was carried out by utilizing a scan rate of 100 mV/s and with a sweep area of between -1 V to 1 V during one test cycle. The same process was repeated by replacing the PPy-Cl/KCl 2 SRE with a commercial double-junction Ag/AgCl reference electrode. Both of these tests would produce a cyclic voltammogram graph as can be seen from Figure 6 below, where the blue line is the cyclic voltammogram graph for the commercial reference electrode and the red line is defined as the cyclic voltammogram graph using PPy-Cl/KCl 2 SRE.

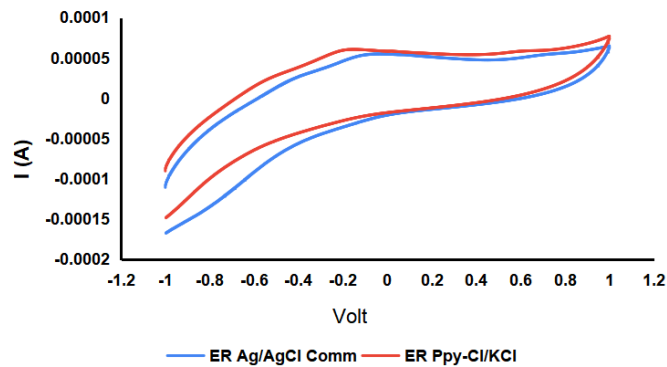


Figure 9. Graph of cyclic voltammogram of commercial Ag/AgCl reference electrode and PPy-Cl/KCl 2 SRE in 0.1M KCl solution.

Referring to Figure 9 above, it was found that the two reference electrodes produced a similar cyclic voltammogram graphic pattern, where this pattern was regarded as a characteristic of carbon electrodes and this is in accordance with the results reported by previous researchers. Carbon electrodes are generally inert. Therefore, neither oxidation nor reduction reactions will occur easily [7,5]. This can be seen from Figure 9, that during the anodic process, there was no clear indication of the peak anodic current (I_{pa}). Similar results were also found during the cathodic process where no peak cathodic current (I_{pc}) was seen [5]. This indicated that the prepared PPy-Cl/KCl 2 SRE showed a non-significantly different performance from the commercial reference electrode, and the PPy-Cl/KCl 2 SRE could function well in the cyclic voltammetry test.

Testing vs Cl Sensor

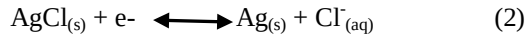
The reference electrode is defined as one of the important components in potentiometric measurements in addition to the working electrode or sensor. The working electrode in potentiometric testing is also known as an ion selective electrode (ISE), because this electrode is considered to be highly selective towards the target ion or ions to be measured. Potentiometric measurement is a type of measurement that is based on measuring the potential difference between the ISE and the reference electrode against the logarithm of the concentration of the test solution, where the resulting potential difference value would correspond to the phenomenon of the Nernst equation below.

$$E = E^0 - \frac{RT}{nF} \ln[a_A] \quad (1)$$

Where E is the value of the potential difference between the reference electrode and the ISE, which is generally obtained from reading the measurement results, and is usually symbolized in millivolt (mV) units. While E^0 is the standard potential energy, R is the ideal gas constant of 8.314

J/K mol, T is the temperature in the K state, n is the number of moles of electrons involved in the study, F is the Faraday number of 96,485 C/mol and $[a_A]$ is the concentration of test solution in uni Molarity (M) [5].

Regarding to this potentiometric measurement concept, the performance test of PPy-Cl/KCl 2 SRE is considered very important to be carried out. In this study, the PPy-Cl/KCl 2 SRE would be paired with a Cl sensor, where the Cl sensor used was Ag/AgCl SPE. The surface of the Ag/AgCl electrode was considered to be very sensitive to the presence of Cl ions from a sample. This could be explained by the mechanism of the AgCl equilibrium system in the aqueous system, where the surface of the solid AgCl would conform to the equilibrium equation as shown from the equation (2):



Having regard to the concept of equilibrium proposed by Le Chartlier, that an equilibrium point would be obtained if the concentration of the right side or products is equivalent to the concentration of the left side or reactants. Thus, equation (2) can be connected to the Nernst equation as follows:

$$E = E^0 - \frac{RT}{nF} \ln \frac{[a_{product}]}{[a_{reactan}]} \quad (3)$$

In this specific matter, as shown in equation (2), Ag and Cl^- act as products, while AgCl acts as a reactant, thus equation (3) above can be converted into equation 4 as follows:

$$E = E^0 - \frac{RT}{nF} \ln \frac{[a_{Ag}][a_{Cl-}]}{[a_{AgCl}]} \quad (4)$$

AgCl is commonly recognized as having low solubility in the aqueous system, so that during the measurement process, AgCl only partially dissolved by releasing Cl ions into the sample. Thus, AgCl is essentially still present in the sample. Therefore, equation (4) can be reduced to the following equation (5):

$$E = E^0 - \frac{RT}{nF} \ln \frac{[a_{AgCl}][a_{Cl-}]}{[a_{AgCl}]} \quad (5)$$

Based on equation 5 above, the concentration of AgCl becomes constant. Thus, equation (5) above can be simplified as follows (6):

$$E = E^0 - \frac{RT}{nF} \ln \frac{[\text{Cl}^-]}{[k]} \quad (6)$$

Because $\ln(10) = 2.303$, equation 6 can be simplified to equation (7) as follows:

$$E = E^0 - \frac{2.303RT}{nF} \text{Log} \frac{[\text{Cl}^-]}{[k]} \quad (7)$$

By substituting the values of R and F into equation (7) above, then at a temperature condition of 298K and for 1 mole of electrons, equation (7) above can be changed to:

$$E = E^0 - 59.16\text{mV} \text{Log}[\text{Cl}^-] + 59.16\text{mV} \text{Log}[k] \quad (8)$$

Because the value of k was constant, the potential value of the Ag/AgCl electrode would depend on changes in the concentration of $[\text{Cl}^-]$ in the test solution. Thus, equation (8) can be simplified to equation (9) as follows:

$$E = E^0 - 59.16\text{mV} \text{Log}[\text{Cl}^-] \quad (9) \quad [9]$$

Consequently, based on equation (9), the ideal value of Nernstian number for Cl sensors based on Ag/AgCl wire electrodes had a value of -59.16 mV for every 10 times decrease in concentration.

In this study, the PPy-Cl/KCl 2 SRE electrode which had been paired with the Ag/AgCl reference electrode (RE) was then connected to an electrochemical workstation for potentiometric measurements. The test solution used in this test was a KCl solution with a concentration of $0.1 - 10^{-4}$ M. The measurement results obtained were then compared with the measurement results of the Ag/AgCl reference electrode pair with the commercial double-junction Ag/AgCl reference electrode. The results of the test versus the Cl sensor can be seen from the data in table 4 and Figure 10 below. From table 4, it was found that both reference electrodes provided values close to the Nernstian number of -57.6 and -54.5 mV/decade, respectively, where this Nernstian number was still within the permissible range for single charged ions, which was amounted to -50 – (-60) mV/decade[10].

Table 4. Performance of Cl vs PPy-Cl/KCl 2 SRE and comm Ag/AgCl sensors in $0.1 - 10^{-4}$ M KCl solution.

Reference Electrode	Slope(mV/dec)	Linear Range (M)	R ²
Comm Ag/AgCl	-57.6	$0.1 - 10^{-4}$	0.9827
PPy-Cl/KCl	-54.5	$0.1 - 10^{-4}$	0.9848

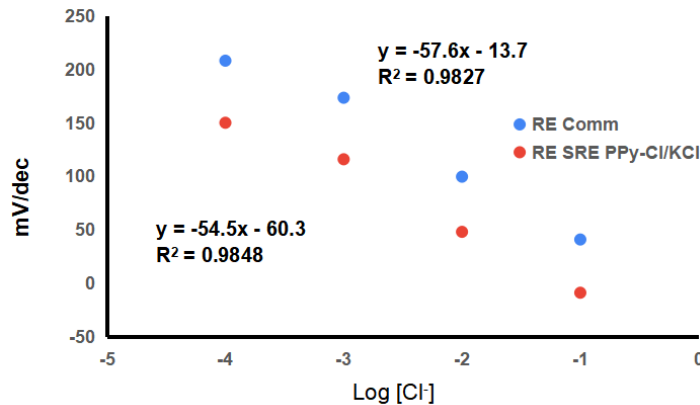


Figure 10. Graph of sensor response of Cl vs PPy-Cl/KCl 2 SRE and comm Ag/AgCl RE in $0.1 - 10^{-4}$ M KCl solution.

However, referring to the data presented in table 4, it was found that the measurement range of the Cl vs PPy-Cl/KCl 2 SRE sensor was shorter than the commercial reference electrode used in this study. This is also reinforced from Figure 10 above, which indicates that the potential value resulting from testing with a solution of 10^{-4} M concentration in PPy-Cl/KCl 2 SRE only had a difference of 21.1 mV/decade with a solution of 10^{-3} M, which means it was beyond -50 – (-60) mV/decade. The short measurement range of the Cl vs PPy-Cl/KCl 2 SRE sensor compared to the commercial reference electrode was caused by the dissolution process of Cl ions from PPy-Cl/KCl 2 SRE into a test sample of 10^{-4} M. At a concentration of 10^{-4} M, the number of ions Cl⁻ in the test solution was relatively small. Through this dissolution process, the test solution was also capable of generating Cl⁻ ions and this caused the accumulation of Cl⁻ ions on the surface of the Cl sensor.

Drift Testing

Drift testing was carried out with the aim of evaluating the potential stability of PPy-Cl/KCl 2 SRE in continuous measurements [6,9]. In this drift test, PPy-Cl/KCl 2 SRE was paired with a double-junction Ag/AgCl reference electrode which was then connected to an electrochemical workstation. Therefore, in this test, PPy-Cl/KCl 2 SRE was used as the working electrode. The data collection process was successfully carried out for one hour continuously in 0.1 M KCl solution. Potential data for 1 hour can be seen in Figure 11 below.

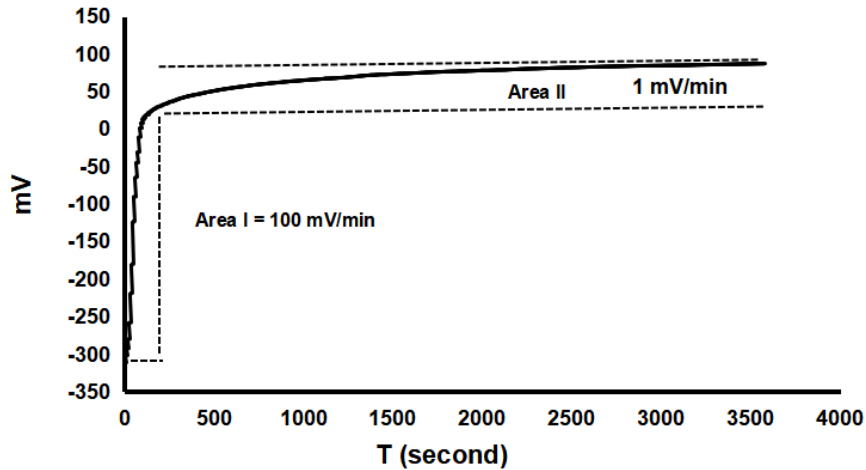


Figure 11. Stability graph of PPy-Cl/KCl 2 SRE vs Ag/AgCl reference electrode in 0.1M KCl solution for 1 hour of measurement.

Based on figure 11, it was found that the potential value was shifted very quickly at the beginning of the test, starting from -313 mV at $t = 0$ seconds and changing to 31 mV at $t = 206.4$ seconds which showed a drift of 100 mV/min. This figure was considered fairly large, where the stability in potentiometric measurements based on theory should not exceed 1 mV/min. However, after $t = 206.4$ seconds, the resulting potential value decreased slowly from 31 mV at $t = 206.4$ seconds to 87 mV at $t = 3581.8$ seconds. This means that the drift had occurred at 1 mV/min and this result is in accordance with the theory [4,6,11].

The high drift value with $t = 206.4$ seconds was caused by the conditioning process of PPy-Cl/KCl 2 SRE, where the condition of PPy-Cl/KCl 2 SRE was still quite dry at the beginning of the test. This may result in the movement of ions either not freely in or out of the PPy-Cl/KCl SRE and still likely to be blocked. However, when the value was above $t = 206.4$ seconds, the movement of the ions began to be free, because in the PPy-Cl/KCl 2 SRE, there was already enough liquid to cause the ions to move [6]. Under these conditions, PPy-Cl/KCl 2 SRE was recommended to be conditioned in aquadest solution for at least 3.5 minutes before being used in the test process.

CONCLUSION

Of the 3 types of PPy-Cl/KCl 2 SRE provided in this study, PPy-Cl/KCl 2 SRE with 15 cycles had been indicated to have characteristics as a reference electrode. It can be found from the results of the ΔmV test which provided a value of < 10 mV which was amounted to 3.43 mV. PPy-Cl/KCl 2 SRE also indicated a fairly good Nernstian number value which was amounted to -54.5 mV/s, although it has a shorter measurement range than the commercial Ag/AgCl reference electrode in the test vs Cl sensor. In tests with cyclic voltammetry, PPy-Cl/KCl 2 SRE produced good performance by providing a voltomogram graph that was almost the same as the commercial Ag/AgCl reference electrode. Moreover, PPy-Cl/KCl 2 SRE also showed a fairly good stability of 1 mV/min, where this stability could be achieved after conditioning for 3.5 minutes.

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