DEVELOPMENT AND CHARACTERIZATION OF SOLID Cu/CuSO₄ REFERENCE ELECTRODES

M. S. Dewi¹*, S. Alva²**, and W. A. W. Jamil²

¹Mechanical Engineering Department, Universitas Mercu Buana, West Jakarta 11650, Indonesia
²Product Development Department, MIMOS Berhad, Technology Park Malaysia, 57000, Kuala Lumpur, Malaysia

Abstract
In this research, a solid Cu/CuSO₄ reference electrode has been developed. In this development process, the Cu/CuSO₄ solid reference electrode provided consists of two types, namely the Cu/CuSO₄ I and the Cu/CuSO₄ II solid reference electrode, abbreviated as ERP Cu/CuSO₄ I and ERP Cu/CuSO₄ II, respectively. ERP Cu/CuSO₄ I was prepared using two layers, namely the Cu/CuSO₄ and the cellulose acetate layers which were placed sequentially on the surface of the planar type Cu electrode. Meanwhile, ERP Cu/CuSO₄ II was prepared using three layers, namely a layer of cotton fiber/cellulose acetate, a layer of Cu/CuSO₄, and a layer of cotton/cellulose acetate placed in sequence on the surface of the planar type Cu electrode, where the CuSO₄ layer is between the two layers of cotton/cellulose acetate. Both types of Cu/CuSO₄ solid reference electrodes were characterized by testing ΔmV in various concentrations of KCl solution and ERP Cu/CuSO₄ II has been produced as the best reference electrode for Cu/CuSO₄ solids with a ΔmV value of 3.3 mV. Furthermore, ERP Cu/CuSO₄ II was selected for characterization using cyclic voltammetry (CV), response vs Cl sensor, and drift testing. In CV testing, ERP Cu/CuSO₄ provides a voltammogram graph pattern similar to the Ag/AgCl as a well-known commercial reference electrode. Meanwhile, in the response vs sensor Cl, the ERP Cu/CuSO₄ II gave a Nernstian number value of -50.1 mV/decade with a test range of 0.1-10⁻³ M. The ERP Cu/CuSO₄ II showed fairly good stability, namely with a drift value of 0.46 mV/minute which is achieved after the conditioning process of 12 minutes.

Keywords: Reference Electrodes, Solids Electrodes, Electrochemical Cells, Ag/AgCl, Cu/CuSO₄

*Corresponding author: Tel. +62 85921414781
E-mail address: shintyamarysca@gmail.com

**Corresponding author: Tel +62 85779381297
E-mail address: sugir.alva@mercubuana.ac.id

1. Introduction
The electrochemical measurement process is one of the most popular measurements and has been applied in many fields including environment [1-2], clinical and pharmaceutical [3], food industry [4], agriculture and fisheries [2], clean water [5], construction [6], chemical synthesis [7], metal plating [8], and oil and gas industry [9]. This is because it has several advantages such as a wide measuring range, in-situ application, not require special skills to run it, not affected by changes in the turbidity and color of the sample, not damage the sample, small sample volume, and is cheap [2-3].

One of the important components in the measurement process by using electrochemical concepts is the reference electrode in addition to the working electrode and the counter electrode. Reference electrodes have main characteristics, namely, their potential value is relatively fixed and not easy to change even though the environmental conditions change. Because of these characteristics, the reference electrode will act as a comparison electrode in the electrochemical measurement processes [3,10-11].

Reference electrodes that are commonly used in the electrochemical measurement process are the saturated calomel electrode (SCE) and the Ag/AgCl electrode. These two reference electrodes have a good stability. However, the SCE electrode has disadvantages such as having toxic chemical components, i.e., a mercury metal. This metal is a dangerous heavy metal. In applications involving high temperatures, the mercury metal found in SCE has the potential to produce a toxic mercuric oxide gas [10]. Meanwhile, the Ag/AgCl electrode has disadvantageous such as the saturated chloride ion solution found on the Ag/AgCl electrode, which often contaminates the sample during the measurement.
process. This can reduce the accuracy of the measurement process. Furthermore, the disadvantage of the SCE and Ag/AgCl electrodes require expensive fabrication cost [12].

The alternative reference electrode of SCE and Ag/AgCl that can be introduced is the Cu/CuSO₄ electrode. This electrode has a potential value of about 337 mV and it uses a CuSO₄ solution as an electrolyte, which is relatively unobtrusive for most types of samples [12-13]. This makes the special advantages of Cu/CuSO₄ electrodes besides being able to be used at high temperatures and a relatively low cost compared to SCE and Ag/AgCl [14].

In general, the Cu/CuSO₄ reference electrode has a tube-like shape and is relatively large. So that for certain applications such as spaciousness measurements which generally require portable and compact devices, this will overcome its constraints when the reference electrode has a large size. Moreover, the current development of measurement devices tends to be smaller and integrated between sensors or detectors with electronic readers (readers) and other modules [3,10]. This makes the size of the Cu/CuSO₄ reference electrode important to be noted.

Meanwhile, research on the development of Cu/CuSO₄ electrodes is still very limited, as carried out by Pirogov et al. [15] which discussed the numerical simulation of Cu/CuSO₄ in the H₂SO₄ system. Other study that conducted by Stern et al [12] was still focused on testing the potential value of the Cu/CuSO₄ reference electrode versus the normal hydrogen electrode (NHE) at various temperature conditions from 5 to 45 °C. Meanwhile, the research conducted by Hall et al. [14] was still focused on developing Cu/CuSO₄ reference electrodes that can be used at high temperatures (around 150 °C) and high-pressure systems. Thus, the three Cu/CuSO₄ reference electrodes that have been previously studied still using the electrodes with conventional shapes. This limited research references make the development of Cu/CuSO₄ challenging for further study and research.

In general, the process of miniaturization or size reduction of the reference electrode is carried out by changing the phase of the existing electrolyte solution from the aqueous or liquid phase to the solid phase as has been done in our previous work with several Ag/AgCl reference electrodes [16-17]. This solid type of electrode has several advantages including a simple fabrication process, can be integrated with sensors and measuring electronic devices, can be mass-produced and low cost. Besides, the size of the electrodes can be adjusted as needed [3,10,16-17]. Therefore, in this work, an initial study was carried out on the development of a low-cost and simple solid type Cu/CuSO₄ reference electrode. In this study, the electrochemical characteristics and performance of the developed solid type of Cu/CuSO₄ reference electrode will also be reported.

2. Method

2.1 Apparatus

The apparatus used in this study are an electrochemical workstation (Corrtest CS350, Corrtest Wuhan Instrument Corp., Ltd.), a double-junction of Ag/AgCl reference electrode (Orion® 900200, Thermo Fisher), 2B type of graphite pencil electrode (GPE, Faber Castell), wire type of Ag/AgCl (provided by MIMOS Berhad, Malaysia), and SPE type of carbon electrodes (Scrint Print BhD, Malaysia).

2.2 Materials

The materials used in this study are CuSO₄ salt (Prima Kimia), copper plate with a thickness of 0.2 mm (LTC Glodok), copper wire, epoxy resin, and hardener (Dextone), KCl salt (Cica-reagent), cellulose acetate (Sigma-Aldrich), Arabic Gum emuligator (Al-Nashr), face cotton (Selection), and acetone solvent (Merck).

2.3 Experiment

2.3.1 Copper Electrode Preparation (Cu Electrode)

The Cu electrode as shown in Figure 1 is provided by employing a copper plate cut to the dimensions of 0.5 cm x 0.5 cm and then on the backside it is connected with a copper wire cable by a soldering process. Furthermore, all the back and edges side of the copper plate to which the cable has been connected are coated with a mixture of epoxy resin and hardener (1 : 1 v/v). After the epoxy resin layer dries and hardens, it is ready to be used as a solid Cu/CuSO₄ reference electrode.

![Cu electrode with dimensions of 0.5 cm x 0.5 cm and a thickness of 0.2 mm](image-url)

2.3.2 Reference Electrode Preparation of Cu/CuSO₄ (ERP Cu/CuSO₄)

A total of two Cu electrodes that have been provided are then carried out by polishing the surface of the electrodes for the cleaning process of the oxide layer that may be present on the electrode surface using...
abrasive paper (grit 120). After the sanding process, the electrodes are wipe with a wet tissue until it clean. After dry and clean, then on the surface of the first Cu electrode evenly coated with 20 μL of CuSO₄ 2 M solution and open drying for about 1 hour. In this study, the solvent from CuSO₄ 2 M solution was 5% (w/v) Arabic gum solution, as it was an ion-free distilled water. After drying and forming a CuSO₄ layer on the surface of the Cu electrode, then the Cu layer was dripped with 20 μL of cellulose acetate solution so that it covered the entire surface of the CuSO₄ layer. Meanwhile, the concentration of cellulose acetate solution used was 5% (w/v) using acetone as a solvent. After the cellulose acetate coating process, the drying process is carried out with a hairdryer over medium heat slowly until the cellulose acetate dries well. After drying, this electrode is then abbreviated as ERP Cu/CuSO₄ I as shown in Figure 2.

Meanwhile, the clean and dry surface of the second Cu electrode was attached with a wet cotton pad which was briefly immersed in 5% (w/v) cellulose acetate solution. Then, the drying process is carried out with a hairdryer over medium heat slowly until the hybrid cotton/cellulose acetate layer dries well. After drying, the surface of the cotton/cellulose acetate hybrid layer was coated with 50 μL of CuSO₄ 2 M solution in 5% (w/v) solvent of Arabic gum. Then, it is allowed to dry at room temperature for 1 hour. After drying, then on the surface of the CuSO₄ layer is attached again with cotton/cellulose acetate fibers as in the previous process and dried over medium heat slowly using a hairdryer until dry. It is then abbreviated as ERP CuSO₄ II, as can be seen in Figure 3.

After the two types of ERP Cu/CuSO₄ have been prepared, the ΔmV KCl response testing process is then carried out, ERP CuSO₄ which has the best ΔmV value will be selected for Cyclic Voltammetric (CV), Cl sensor, and drift testing.

3. Results and Discussion

3.1 ΔmV KCl response

The main characteristic of a reference electrode is that it has a stable potential value despite changes in the sample environment such as sample concentration [3,11]. The stability of a reference electrode cannot be separated from the use of electrolyte salts in large concentrations. In the Cu/CuSO₄ reference electrode, the electrolyte used is CuSO₄ salt with a concentration of 2 M. By the concept of Le Chatelier’s principle of equilibrium [10,18], the high concentration of the electrolyte used causes the equilibrium to slowly move from the reference electrode to the sample to reach a new equilibrium point, where the sample concentration is usually lower. This leaves the sample with almost no potential change on the surface of the reference electrode [10].

Therefore, it is the crucial reason of ΔmV Cl ion response that should be carried out. In testing the two types of ERP Cu/Cu/CuSO₄ that have been provided previously were tested using variations in the concentration of KCl solution with a range between 0.1 – 10⁻⁴ M. The Cu/Cu/CuSO₄ will have a function as a working electrode. Furthermore, the two electrodes, namely ERP Cu/CuSO₄ and the reference electrode are connected to an electrochemical workstation and recorded the mV number generated from each test under KCl solution. The results of the ΔmV test are presented in Table 1 and Figure 4.

Table 1. Value of ΔmV ERP Cu/CuSO₄ I and II in various concentrations of KCl solution

| Log[KCl] | ERP Cu/CuSO₄ I (mV) | ERP Cu/CuSO₄ II (mV) |
|----------|---------------------|----------------------|
| -1       | -218.5              | 62.7                 |
| -2       | -235.0              | 63.9                 |
| -3       | -227.1              | 66.0                 |
| -4       | -246.1              | 65.3                 |
| ΔmV KCl  | 27.6                | 3.3                  |

Fig. 2. Photograph of ERP Cu/CuSO₄ I (a), Design of cross section view of ERP Cu/CuSO₄ I configuration (b)

Fig. 3. Photograph of ERP Cu/CuSO₄ II (a), Design of cross section view of ERP Cu/CuSO₄ II configuration (b)
It can be seen from Table 1 and Figure 4 that ERP Cu/CuSO\textsubscript{4} II has the lowest $\Delta mV$ KCl, which is 3.3 mV. This indicates that ERP Cu/CuSO\textsubscript{4} II has characteristics as a reference electrode, where even though the KCl concentration changes, the potential value generated by ERP Cu/CuSO\textsubscript{4} is quite stable. This is in contrast with that shown by ERP Cu/CuSO\textsubscript{4} I which produces $\Delta mV$ KCl higher than 12 mV, i.e., 27.6 mV, where the reference electrode standard is not allowed to produce KCl response exceeding 12 mV\textsuperscript{3}. Thus, ERP Cu/CuSO\textsubscript{4} II is the optimum one and selected for further testing.

The high $\Delta mV$ value of ERP Cu/CuSO\textsubscript{4} I can be explained as follow, it cannot be separated from the ERP design itself, where the Cu/CuSO\textsubscript{4} ERP uses only two membrane layers, i.e., CuSO\textsubscript{4} layer and cellulose acetate as shown in Figure 2. The CuSO\textsubscript{4} layer itself consists of two components, namely CuSO\textsubscript{4} crystals and Arabic gum, where CuSO\textsubscript{4} act as an electrolyte [12,14], while Arabic gum as an emulgator [19] and as a supporting matrix for placing CuSO\textsubscript{4} crystals right above the electrode surface Cu. Arabic gum is a polysaccharide that is very soluble in water and forms a hydrogel [16,20]. This causes the ions from both the sample and the Cu/CuSO\textsubscript{4} ERP to still move properly. The basis for selecting Arabic gum is also based on the ability to reduce the corrosion process on the Cu electrode surface, where it is well known that Arabic gum is a natural rust inhibitor [21].

However, the nature of Arabic gum which is very water-soluble also has its effects. During the measurement period, the sample solution that entered the membrane layer on the ERP Cu/CuSO\textsubscript{4} I surface had made Arabic gum binds the CuSO\textsubscript{4} crystal salt to expand and pushed the protective layer, namely the cellulose acetate layer [3,16]. This causes the membrane layer to break so that the sample solution can contact directly at the surface of the Cu electrode and the CuSO\textsubscript{4} crystalline salt also dissolves and releases into the sample as illustrated in Figure 5. This causes the potential value on the surface of the Cu electrode to change.

Meanwhile, the stability of the CuSO\textsubscript{4} II ERP can be explained due to the CuSO\textsubscript{4} salt that dissolved in Arabic gum being trapped in the cotton/cellulose acetate membrane layer either on the surface of the Cu electrode or on the protective layer of the cotton/cellulose acetate membrane. This facilitate to reduce the internal pressure when the gum begins to expand during the measuring process. Also, the presence of a protective layer of the cotton/cellulose acetate membrane on the surface also contributes to preventing the sample from re-direct contact with the Cu electrode surface. Meanwhile, the presence of a protective layer of the cotton/cellulose acetate strong membrane helps to reduce the rapid and excessive release of CuSO\textsubscript{4} salts into the sample, as shown in Figure 6. This makes ERP CuSO\textsubscript{4} II less susceptible to potential changes during the measurement process of a sample such as variations in the concentration of KCl [3].

### 3.2 Cyclic Voltammetry (CV)

CV testing is one type of testing in electrochemistry. This test can describe a mechanism of reduction and oxidation (redox) reactions from the surface of a test material. The implementation of CV testing will involve three electrodes which include working electrodes, reference electrodes, and auxiliary electrodes or also known as counter electrodes [22]. This is the reason why CV testing is important to carry out, where the aim is to see the performance of the Cu/CuSO\textsubscript{4} ERP developed whether it has the same capability as a commercial reference electrode.

In this test, the ERP Cu/CuSO\textsubscript{4} II that has been prepared will be paired with an SPE type carbon electrode which acts as a working electrode, and EGP as an auxiliary electrode. The three electrodes will be
connected to an electrochemical workstation and immersed in a 0.1 M KCl solution as a test solution. The CV testing process is carried out using a scan rate of 100 mV/s and a swept area between -1 to 1 V during one test cycle. The same process was repeated by replacing ERP Cu/CuSO$_4$ II with a commercial two-bridge type Ag/AgCl reference electrode. These two tests will produce a cyclic voltammogram graph as can be seen from Figure 7 below, where the blue line is the cyclic voltammogram graph for the commercial reference electrode and the brown graph is a cyclic voltammogram graph using ERP Cu/CuSO$_4$ II.

**Figure 7. Cyclic voltammogram graph of commercial Ag/AgCl reference electrodes and ERP Cu/CuSO$_4$ in 0.1M KCl solution**

Based on Figure 7, it can be seen that the two reference electrodes produce a similar cyclic voltammogram graphic pattern, where this pattern is characteristic of the carbon electrode and this is similar results reported by previous researchers [11]. One of the basic properties of the carbon electrode is that it is inert, so it is not easy to experience oxidation or reduction reactions [10-11]. This can be seen from Figure 7, that during the oxidation process (anodic process), no clear peak anodic current (Ipa) was seen, except for the commercial reference electrode, there was a slight peak in Ipa in the 0.12 V area with an Ipa value of 1.56 $\mu$A/cm$^2$. The appearance of this small Ipa peak is more due to impurities from the binder contained in the carbon in the SPE. The same thing happened during the reduction process (cathodic process), no peak cathodic current (Ipc) was seen [21]. This indicates that the ERP Cu/CuSO$_4$ II prepared shows a performance that is not much different from the commercial reference electrodes and ERP Cu/CuSO$_4$ II performs well in cyclic voltammetric tests.

3.3 Testing vs Sensor Cl
The reference electrode is an important component in potentiometric measurements in addition to the working electrode or sensor. The working electrode in potentiometric testing is also known as the ion-selective electrode (ISE) because this electrode is very selective about the target ion or ion to be measured. Potentiometric measurement is a measurement based on the measurement of the potential difference between the ESI and the reference electrode against the logarithm of the concentration of the test solution, where the value of the resulting potential difference follows the phenomenon of the Nernst equation below:

$$E = E^0 - \frac{2.303RT}{nF} \log \left[ \frac{a_A}{a_B} \right]$$  \hspace{1cm} (1)

where $E$ is the value of the potential difference between the reference electrode and the ESI which is generally obtained from the reading of the measurement results and usually uses the millivolt (mV) unit. While $E^0$ is the standard potential energy, $R$ is the ideal gas constant of 8.314 J/K mole, $T$ is the temperature in the K, $n$ is the number of moles of electrons involved in the reaction, $F$ is the Faraday number of 96,485 C/mole and $[a_A]$ is the concentration of the test solution in the unit of molarity (M) [11].

Based on this potentiometric measurement concept, testing the ERP performance of Cu/CuSO$_4$ is important to do. In this study, ERP Cu/CuSO$_4$ II will be paired with the Cl sensor, where the Cl sensor used is an Ag/AgCl wire electrode. The surface of the Ag/AgCl electrode is known to be very sensitive to the presence of Cl ions from a sample. This can be described by the mechanism of the AgCl equilibrium system in the aqueous system, where the surface of the AgCl solid will follow the equilibrium equation as shown in equation (2):

$$\text{AgCl(s)} + e^- \leftrightarrow \text{Ag(s)} + \text{Cl}^-_{(aq)}$$ \hspace{1cm} (2)

Based on the concept of equilibrium raised by Le Chatelier’s principle [10,18], that an equilibrium point will be realized if the concentration of the right side or product is equivalent to the concentration of the left side of the reactants. Thus, equation (2) can be related to the Nernst equation to be:

$$E = E^0 - \frac{2.303RT}{nF} \log \left[ \frac{a_{\text{produkt}}}{a_{\text{reaktan}}} \right]$$ \hspace{1cm} (3)

In this case, as shown by equation (2) which acts as a product are Ag and Cl$, while AgCl acts as a reactant, thus equation (3) above can be converted into equation 4 as follows:

$$E = E^0 - \frac{2.303RT}{nF} \log \left[ \frac{a_{\text{Ag}}a_{\text{Cl}^-}}{a_{\text{AgCl}}} \right]$$ \hspace{1cm} (4)
AgCl is known to have low solubility in the aquatic system, so that during the measurement process, AgCl only partially dissolves by releasing Cl ions into the sample, so basically AgCl is still present in the sample. Therefore, equation (4) can be reduced to equation (5) as follows:

\[ E = E^0 - \frac{2.303RT}{nF} \log \left[ \frac{[\text{AgCl}]}{[\text{Ag}]} \right] \]  

(5)

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

\[ E = E^0 - \frac{2.303RT}{nF} \log \left[ \frac{[\text{Cl}^-]}{[k]} \right] \]  

(6)

By substituting the R and F values into equation (6) above, then at the temperature conditions of 298 K and for 1 mole of electrons, equation (6) above can be changed to:

\[ E = E^0 - 59.16 \text{mV} \log[\text{Cl}^-] + 59.16 \text{mV} \log[k] \]  

(7)

Because the value of \( k \) is constant, the potential value of the Ag/AgCl electrode will depend on the change in the concentration of [Cl\(^-\)] in the test solution. Thus, equation (7) can be simplified into equation (8) as follows:

\[ E = E^0 - 59.16 \text{mV} \log[\text{Cl}^-] \]  

(8) \[ \text{[16]} \]

Thus, based on equation (8), the ideal value of the Nernstian number for a Cl sensor based on the Ag/AgCl wire electrode has a value of -59.16 mV for every 10 times the decrease in concentration.

In this study, the ERP Cu/CuSO\(_4\) II electrode which has been paired with the Ag/AgCl wire electrode is then connected to an electrochemical workstation for potentiometric measurements. The test solution used in this test is a KCl solution with a concentration of 0.1 – 10\(^{-4}\) M. The measurement results obtained are compared with the measurement results of the Ag/AgCl wire electrode pair with the commercial Ag/AgCl two bridge type reference electrodes. The test results versus the Cl sensor can be seen from the data table 2 and Figure 8 below. It can be seen from Table 2 that the two reference electrodes provide values that are close to the Nernstian number, namely -53.7 and -50.1 mV/ decade, respectively, where this Nernstian number is still by the range justified for single charged ions, namely of -50 - (-60) mV/ decade [23].

### Table 2. The performance of the Cl vs ERP Cu/CuSO\(_4\) II and ER Ag/AgCl comm sensors in a 0.1 - 10\(^{-4}\) M KCl solution.

| Reference Electrode | Slope (mV/decade) | Linear Range (M) | \( r^2 \) |
|---------------------|-------------------|-----------------|-----------|
| Ag/AgCl Comm        | -53.7             | 0.1 – 10\(^{-4}\) | 0.9992    |
| Cu/CuSO\(_4\) II    | -50.1             | 0.1 – 10\(^{-3}\) | 0.9820    |

However, if it is seen based on the data presented in Table 2, it can be seen that the measurement range of the Cl vs ERP Cu/CuSO\(_4\) II sensors are shorter than the commercial reference electrodes used in this study. This is also reinforced from Figure 8 above. It can be seen that the potential value resulting from testing with a solution of 10\(^{-4}\) M KCl concentration on ERP Cu/CuSO\(_4\) II is only 21.1 mV/decade different from the 10\(^{-3}\) M solution, which means that it is outside -50 - (-60) mV/decade. The short measurement range of the Cl vs ERP Cu/CuSO\(_4\) II sensors compared to the commercial reference electrodes is due to the dissolution process of SO\(_4^{2-}\) ions from ERP Cu/CuSO\(_4\) II into the 10\(^{-4}\) M test sample. At a concentration of 10\(^{-4}\) M, the number of Cl ions in the test solution is a little. With this dissolving process, the test solution also forms SO\(_4^{2-}\) ions and this causes competition between Cl\(^-\) and SO\(_4^{2-}\) ions on the surface of the Cl sensor. Based on reports provided by previous researchers, the presence of SO\(_4^{2-}\) 100 times higher than Cl ions in the test solution that can seriously interfere with the response of the Cl sensor type of Ag/AgCl wire electrode [3].

### 3.4 Drift Testing

The drift testing is carried out to confirm the potential stability of the Cu/CuSO\(_4\) II ERP in a continuous measurement [10,16]. In this drift test,
ERP Cu/CuSO₄ II is paired with a two-bridge type Ag/AgCl reference electrode which is then connected to an electrochemical workstation, so that in this test, ERP Cu/CuSO₄ functions as a working electrode. The data collection process was carried out for one hour in a row in a 0.1 M KCl solution, where the potential data for 1 hour can be seen in Figure 9.

From Figure 9, it can be seen that at the beginning of the test the potential value moves very quickly, starting from -26 mV at t = 0 second and changing to 4.8 mV at t = 712.4 seconds, which means there is a drift of 2.6 mV/minute. This figure is quite large, where the stability of the potentiometric measurement is theoretically not to exceed 1 mV/minute. However, after t = 712.4 seconds, the resulting potential value gradually drops from 4.8 mV at t = 712.4 seconds to -17.3 mV at t = 3581.8 seconds. This means that the drift that occurs is 0.46 mV/minute and this is still lower than 1 mV/minute [10-11,24].

The high drift value up to t = 712.4 seconds was caused by the conditioning process of ERP Cu/CuSO₄ II, where at the beginning of the test, the Cu/CuSO₄ II ERP conditions were still quite dry. This causes the movement of ions either out of or out of ERP Cu/CuSO₄ II is still not free and experience obstacles. However, after the above t = 712.4 seconds the ion movement begins to free because in ERP Cu/CuSO₄ II there is enough liquid to cause the ions to move [10]. Under these conditions, it is recommended that ERP Cu/CuSO₄ II be conditioned in a distilled water solution for at least 12 minutes before being used in the testing process.

### 4. Conclusions

The two types of Cu/CuSO₄ solid reference electrodes provided in this study, the ERP Cu/CuSO₄ II has shown characteristics as a good reference electrode. This can be seen from the Δm V test which has a value lower than 12 mV, i.e., 3.3 mV. Meanwhile, the ERP Cu/CuSO₄ I did not show the characteristics of a reference electrode by producing an Δm V value of 27.6 mV. The ERP Cu/CuSO₄ II also provides a fairly good Nernstian number value of -50.1 mV/decade, although it has a shorter measurement range compared to the commercial Ag/AgCl reference electrode on the CI response. From the cyclic voltammetry test, the ERP Cu/CuSO₄ II produced a good performance by producing a line plot that similar with the commercial Ag/AgCl reference electrode. The ERP Cu/CuSO₄ II also showed fairly good stability, namely 0.46 mV/minute, where this stability was achieved after conditioning for 12 minutes.

### 5. Acknowledgments

The authors thanks to the Postgraduates Studies of Master of Mechanical Engineering of Mercu Buana University who supported for completion this research through the use of material laboratory and facilities.

### References

[1] S. Alva, A. Widinugroho, M. Adrian, D. S. Khaerudini, S. E. Pratiwi, and A. S. A. Aziz, “The New Lead (II) Ion Selective Electrode Based On Free Plasticizer Film of pTHFA Photopolymer,” *J. Electrochem. Soc.*, vol. 166, no. 15, pp. B1513–B1519, 2019, doi: 10.1149/2.0601915jes.

[2] S. Alva, R. Suherman, V. Frialiandita, D. S. Khaerudini, E. H. Majlan, and A. S. A. Aziz, “Preliminary study of poly(Tetrahydrofurfuryl acrylate) thin film as a potential material of ion selective electrodes: The case of nitrate ion-selective electrode,” *Indones. J. Chem.*, vol. 20, no. 3, pp. 645–654, 2020, doi: 10.22146/ijc.44478.

[3] S. Alva,, E. Hindasah, W. A. W. Jamil, T. Prasetyorini, “Development of Integrated Planar Chloride Ion-Selective Electrode and Ag/AgCl Reference Electrode based on Chitosan/Cellulose Acetate Membrane for Blood Serum Analysis,” *Anal. Bioanal. Electrochem.*, vol. 11, no. 12, pp. 1669-1686, 2019

[4] A. Sudarvizhi, K. Pandian, O. S. Oluwafemi, and S. C. B. Gopinath, “Amperometry detection of nitrite in food samples using tetrasulfonated copper phthalocyanine modified glassy carbon electrode,” *Sensors Actuators, B Chem.*, vol. 272, pp. 151–159, 2018, doi: 10.1016/j.snb.2018.05.147.

[5] A. Izadyar, F. Al-Amoody, and D. R.
Arachchige, “Ion transfer stripping voltammetry to detect nanomolar concentrations of Cr (VI) in drinking water,” *J. Electroanal. Chem.*, vol. 782, pp. 43–49, 2016, doi: 10.1016/j.jelechem.2016.10.002.

[6] V. Maruthapandian, V. Saraswathy, and S. Muralidharan, “Development of solid state embeddable reference electrode for corrosion monitoring of steel in reinforced concrete structures,” *Cem. Concrr. Compos.*, vol. 74, pp. 100–108, 2016, doi: 10.1016/j.cemconcomp.2016.09.001.

[7] S. Liang and C. C. Zeng, “Organic electrochemistry: Anodic construction of heterocyclic structures,” *Curr. Opin. Electrochem.*, vol. 24, pp. 31–43, 2020, doi: 10.1016/j.joelec2020.06.005.

[8] P. Huang and Y. Zhang, “Electrodeposition of nickel coating in choline chloride-urea deep eutectic solvent,” *Int. J. Electrochem. Sci.*, vol. 13, no. 11, pp. 10798–10808, 2018, doi: 10.20964/2018.11.65.

[9] R. F. Wright, P. Lu, J. Devkota, F. Lu, M. Ziemek-Moroz, and P. R. Ohodnicki, “Corrosion sensors for structural health monitoring of oil and natural gas infrastructure: A review,” *Sensors*, vol. 19, no. 18, 2019, doi: 10.3390/s19183964.

[10] S. Alva, D. Ardiyansyah, D. S. Khaerudini, and R. Suherman, “Solid-State Reference Electrode Based on Thin-Films of Tetrahydrofurfuryl Acrylate (pTHFA) Photopolymer,” *J. Electrochem. Soc.*, vol. 166, no. 8, pp. B598–B603, 2019, doi: 10.1149/2.1331906jes.

[11] S. Alva, A. Aziz, M. I. Syono, and D. Sebayang, “Development of solid-state reference electrode based on sodium polyanethol sulfonate immobilised on cellulose acetate,” *J. Phys. Sci.*, vol. 28, no. 2, pp. 161–179, 2017, doi: 10.21315/jps2017.28.2.11.

[12] H. A. G. Stern, D. R. Sadoway, and J. W. Tester, “Copper sulfate reference electrode,” *J. Electroanal. Chem.*, vol. 659, no. 2, pp. 143–150, 2011, doi: 10.1016/j.jelechem.2011.05.014.

[13] S. Szabó and I. Baksó, “Reference electrodes in metal corrosion,” *Int. J. Corros.*, vol. 2010, 2010, doi: 10.1155/2010/756950.

[14] D. M. Hall, J. R. Beck, E. Brand, M. Ziemek-Moroz, and S. N. Lvov, “Copper-Copper Sulfate Reference Electrode for Operating in High Temperature and High Pressure Aqueous Environments,” *Electrochim. Acta*, vol. 221, pp. 96–106, 2016, doi: 10.1016/j.electacta.2016.10.143.

[15] B.Y. Pirogov, and A.G. Zelinsky, “Numerical simulation of electrode process in Cu/CuSO4 + H2SO4 system,” *Electrochim. Acta*, vol. 49, pp. 3283–3292, 2004.

[16] S. Alva, A. S. Binti Abdul Aziz, M. I. Bin Syono, and W. A. Bin Wan Jamil, “Ag/AgCl reference electrode based on thin film of arabic gum membrane,” *Indones. J. Chem.*, vol. 18, no. 3, pp. 479–485, 2018, doi: 10.22146/ijjchem.28859.

[17] S. Alva, L. Y. Heng, and M. Ahmad, “Optimization of Screen Printed Reference Electrode Based on Charge Balance and Poly (Butyl Acrylate) Photocurable Membrane,” *Int. J. Innov. Mech. Eng. Adv. Mater.*, vol. 2, no. 1, p. 10, 2016, doi: 10.22441/ijimeam.2016.1.002.

[18] S.Ebrahimi and D. J. Roberts, “Bioregeneration of single use nitrate selective ion-exchange resin enclosed in a membrane: Kinetics of desorption,” *Sep. Purif. Technol.*, vol.146, pp.268-275, 2015, doi: https://doi.org/10.1016/j.seppur.2015.03.038

[19] S. Sethuraman and K. Rajendran, “Is Gum Arabic a Good Emulsifier Due to CH...πInteractions? How Urea Effectively Destabilizes the Hydrophobic CH...πInteractions in the Proteins of Gum Arabic than Amides and GuHCl?,” *ACS Omega*, vol. 4, no. 15, pp. 16418–16428, 2019, doi: 10.1021/acsomega.9b01980.

[20] B. Singh, S. Sharma, and A. Dhiman, “Acacia gum polysaccharide based hydrogel wound dressings: Synthesis, characterization, drug delivery and biomedical properties,” *Carbohydr. Polym.*, vol. 165, pp. 294–303, 2017, doi: 10.1016/j.carbpol.2017.02.039.

[21] I. G. A. Arwati *et al.*, “Kesan Pemendapan Elektroforesis Gam Arab terhadap Halaju Kakisan pada Aluminium 5052,” *Sains Malaysiana*, vol. 48, no. 2, pp. 401–406, 2019, doi: 10.17576/jsm-2019-4802-18.

[22] N. Elgrishi, K. J. Rountree, B. D. McCarthy, E. S. Rountree, T. T. Eisenhart, and J. L. Dempsey, “A Practical Beginner’s Guide to Cyclic Voltammetry,” *J. Chem. Educ.*, vol. 95, no. 2, pp. 197–206, 2018, doi: 10.1021/acs.jchemed.7b00361.

[23] D. S. Khaerudini, F. Rahman, and S. Alva, “Optimization strategy of Ag/AgCl thin film electrodes approached by chlorination process
for electrochemical response materials,”
*Mater. Chem. Phys.*, vol. 240, no. 1, p. 122294, 2020, doi: 10.1016/j.matchemphys.2019.122294.

[24] K.S.Ying, L.YHeng, N.I.Hassanan, S.A.Hasbullah,” A New and All-Solid-State Potentiometric Aluminium Ion Sensor for Water Analysis,” *Sensors* vol. 20, pp. 6898, 2020.