



CHLORIDE SENSOR FABRICATION BASED ON SPE Ag/AgCl THROUGH CYCLIC VOLTAMMETRIC TECHNIQUE: SCAN RATE EFFECT

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Abstract

The Cyclic Voltammetric (CV) technique is one of the Ag/AgCl fabrication processes. In electrochemical processes using this CV technique, the microstructure of the surface of a substrate or electrode can affect the scan rate. Thus, this study aims to identify the scan rate effect of the Cl-ion sensor fabrication process using the CV technique on the performance of the Cl-ion sensor. First, the CV process was carried out in one cycle to grow the AgCl layer on the Ag surface. Then, this process was carried out at varied scan rates of 20, 40, 60, 80, and 100 mV/s. After completing the Ag/AgCl fabrication process, it was followed by the characterization process, selectivity coefficient test, lifetime test, and validation test to compare the test results of the Cl SPE Ag/AgCl ion sensor with Ag/AgCl commercial. The results showed that the optimum Cl-ion sensor response was obtained at the scan rate of 60 mV/s. Then, based on the validation test, the Cl-ion in the two samples did not show significant differences. Therefore, it indicates that the SPE Ag/AgCl ion sensor has the same performance as the Ag/AgCl commercial.

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INTRODUCTION

Chloride ion (Cl⁻ions) is one of the most common types of anions and is typically found in many types of samples such as seawater, electrolyte body fluids, soil, drinking water, and rocks [1, 2, 3, 4, 5]. Besides, Cl⁻ions are widely applied daily for medicine, food, energy, chemical synthesis, and others [6, 7, 8, 9]. However, the presence of Cl⁻ions in an inappropriate amount negatively affects living things and the environment. Thus, monitoring Cl⁻ions in a sample is important [2, 4, 10, 11, 12].

Some methods for measuring Cl⁻ions have been developed and applied, such as titration, ion chromatography, ICP-AES, and UV-Vis. However, they have some disadvantages such as requiring a long time, unable to perform in situ measurements, limited measurement range, requiring special treatment, and being costly [2]. Another alternative is using the potentiometric measurement technique, which is based on measuring the potential difference between the

working electrode and the reference electrode versus the ion concentration log. The measurement process with the potentiometric technique is performed in the absence of current [13]. The advantages of this method cover in-situ measurement, fast, minimum treatment, wide measurement range, and low cost [14].

The working electrode used in the potentiometric technique is widely known as the ion-selective electrode (ISE), which acts as a sensor. This electrode has a thin layer that is sensitive to the presence of target ions [13]. One of the most common types of ISE used in testing Cl⁻ions is the Ag/AgCl electrode. The surface of the Ag/AgCl electrode is very sensitive to changes in the concentration of Cl⁻ions in a sample [2, 10, 11, 15, 16]. In general, the Ag/AgCl electrode shape is like a rod and large. This shape and size make the Ag/AgCl electrode less effective as it requires a large sample volume and is costly. Besides, this shape and size provide complexity in the integration process with other electrodes such

as reference electrodes or electronic reading devices. Thus, making Ag/AgCl electrodes in smaller and simpler sizes [2, 10, 15].

One type of ISE electrode that has developed over the decades is the screen-printed electrode (SPE). The advantages of this electrode are small, simple, easy to integrate with other electrodes or electronic reading devices, has low sample volume, and is low cost. Therefore, it is more flexible for in-situ measurements [2][11].

Generally, the Ag/AgCl electrodes are fabricated through some methods such as the oxidation process with solvents and electrochemical processes such as asymmetric square wave voltammetry (aSWV), open current potential (OCP), or anodization process at certain voltages [2, 10, 16, 17]. Besides, the Ag/AgCl fabrication process using the Cyclic Voltammetric (CV) technique has also been previously carried out but only at one scan rate [18]. However, in electrochemical processes using CV techniques, the scan rate can affect the microstructure of the surface of a substrate or electrode [19]. Thus, it has the potential to affect the performance of the resulting Cl⁻ ion sensor. Therefore, this study aims to identify the effect of the scan rate of the Cl⁻ ions sensor fabrication process using the CV technique on the performance of the Cl⁻ ion sensor.

METHOD

Instrumentations

The implementation of this research used some equipment, including the CS350-Corrtest electrochemical workstation (Wuhan Corrtest Instruments Corp., Ltd., Wuhan, China). The reference electrode of Ag/AgCl double-junction type Orion®900200 from Thermo Fischer, the Ag/screen-printed electrode (SPE) (Sprint Print Berhad, Malaysia) is shown in Figure 1, where Ag and C electrodes with the diameter of 4 mm and thickness of 10 mm of each. Meanwhile, the commercial Cl sensor used was the rod type Ag/AgCl electrode (model E207, Warner Instruments).

Material

The materials used were salts of KCl, Na₂CO₃, Na₂SO₄, 10H₂O, Na₂HPO₄, 12H₂O and

NaH₂PO₄, 2H₂O (Cica Reagents). It also used salt of KNO₃ (Merck).

Experimental

The SPE Ag/C and the double junction Ag/AgCl electrode were connected to a CS350-Corrtest electrochemical workstation. The Ag electrode acted as the working electrode, while the C electrode served as the counter electrode and the Ag/AgCl electrode became the reference electrode. The three electrodes were then rinsed with deionized water (DIW) and dried with tissue paper. After drying, they were put in a 0.1 M KCl solution and followed by the CV process for one cycle to grow the AgCl layer on the Ag surface. This process was carried out at varied scan rates of 20, 40, 60, 80, and 100 mV/s. After the CV process was conducted, the AgCl layer was formed on the Ag surface marked by a change from silver to dark gray color [2][16], as shown in Figure 2.

Then, the produced SPE Ag/AgCl electrode acted as Cl⁻ ion sensors and characterization were carried including testing the response of Cl⁻, Nernst number, linear range, and LOD using 0.1-10⁻⁸ M KCl solution. Then, it was followed by the selectivity coefficient test using the separated solution methods (SSM). It used the interfering solution of NO₃⁻, H₂PO₄⁻, HPO₄²⁻, SO₄²⁻ and CO₃²⁻ in which the main ion solution and the interfering ion were carried out at a concentration of 0.1 M. Furthermore, it was also followed by the lifetime test of the Cl⁻ ion sensor and validation test using a real sample solution, where the test results of the Cl SPE Ag/AgCl ion sensor would be compared with the test using the Ag/AgCl commercial. The whole characterization process was carried out using potentiometric measurement techniques. The Ag/AgCl electrode, both SPE and commercial, served as the working electrode and the double junction Ag/AgCl electrode served as the reference electrode. The working electrode and the reference electrode were connected to the electrochemical workstation and included in the test solution in the testing process. The obtained potential value (mV) is then recorded to be grouped and calculated.

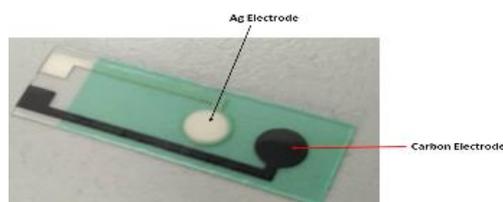


Figure 1. SPE Ag/C from Sprint Print Berhad-Malaysia

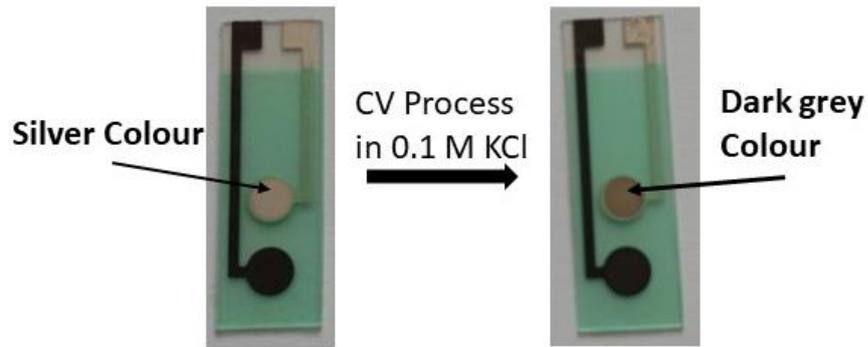


Figure 2. Formation of the Ag/AgCl layer on the Ag surface after CV process for 1 cycle at 0.1 M KCl solution

RESULTS AND DISCUSSION

Chloride Sensor Preparation

The CV technique's electrodeposition process is common to coat a metal surface [10,18,19]. In this study, the AgCl coating process on the surface of SPE Ag to form the Cl⁻ ion sensor was performed at varied scan rates and 0.1 M KCl solution for one cycle. Figure 3 shows the process of forming the AgCl layer on the surface of the SPE Ag electrode at the scan plot from -1 to 1 V, in which the voltage of -1 to +1 V was the occurrence of the AgCl coating process on the SPE Ag surface where the Ag metal reacts with Cl⁻ ions resulting AgCl and one electron. The occurrence area of the coating was defined as an anodic process. Meanwhile, after it reached +1 V, it would return to -1 V in which there was a partial dissolution of the AgCl layer, where the AgCl layer

reacts with one electron to form Ag metal and Cl⁻ ions. The area of dissolution of AgCl was defined as the cathodic area [10, 19, 20]. The overall reaction process for the formation of the AgCl layer on the SPE Ag surface followed the reaction equation:



Figure 3 shows that the oxidation (*I_{pa}*) and reduction (*I_{pc}*) peaks are different for each scan rate variation.

In general, the *I_{pa}* and *I_{pc}* peaks would be linear with the applied scan rate [19][21]. This is because the *I_{pa}* and *I_{pc}* peaks represent the maximum current for the oxidation and reduction processes during the electrodeposition process.

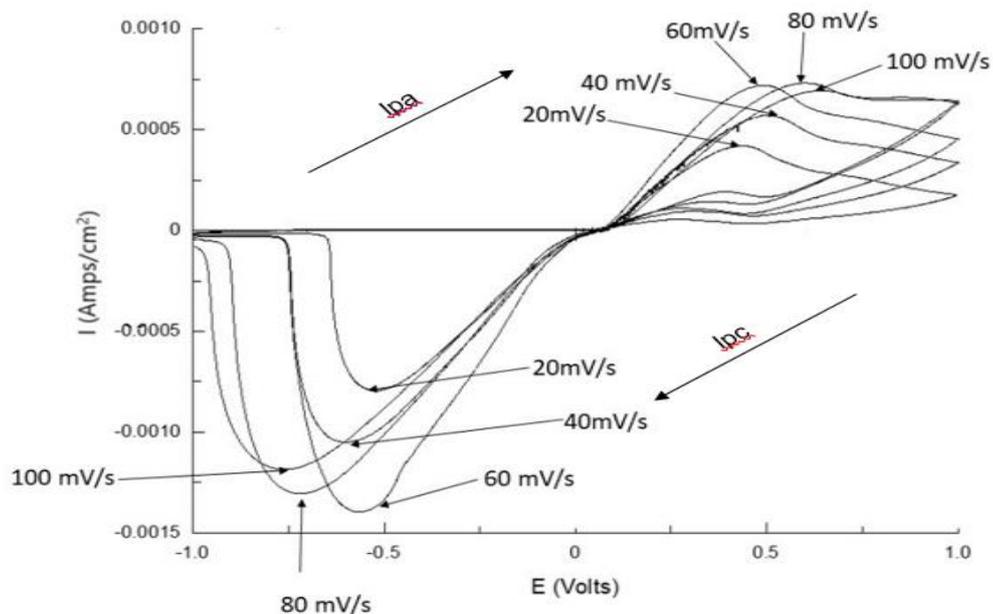


Figure 3. Cyclic voltammetry graph of Ag/AgCl formation process at 0.1 M KCl solution with varied scan rates

However, Figure 3 and Figure 4 show that the I_{pa} and I_{pc} peaks were linear only from 20 mV/s to 60 mV/s. Meanwhile, the scan rates of 80 mV/s and 100 mV/s produced static and decreasing I_{pa} peaks. Even after the I_{pc} peak, it became higher as shown in Table 1 and Figure 4.

Table 1. The peak values of I_{pa} , I_{pc} , and I_{pa}/I_{pc} on the scan rate variation of the AgCl formation process on the SPE Ag surface

SR (mV/s)	I_{pa} (A/cm ²)	I_{pc} (A/cm ²)	I_{pa}/I_{pc}
20	4.14×10^{-4}	-7.80×10^{-4}	0.53
40	5.58×10^{-4}	-1.05×10^{-3}	0.53
60	7.01×10^{-4}	-1.38×10^{-3}	0.51
80	7.27×10^{-4}	-1.29×10^{-3}	0.56
100	6.84×10^{-4}	-1.17×10^{-3}	0.58

The I_{pa} and I_{pc} peaks, which are not linear at 80 and 100 mV/s are caused by the thicker AgCl layer formed, where the AgCl layer tends to be an insulator. Therefore, the maximum current at 80 and 100 mV/s tends to decrease due to increasing resistance [16][22]. Besides, Figure 3 shows that the process of AgCl formation through the CV technique took place with an irreversible process by producing different forms of oxidation and reduction peaks, and it was reinforced from the absolute value of $I_{pa}/I_{pc} \neq 1$ as shown in Table 1, in which the reversible reaction has the absolute value of I_{pa}/I_{pc} of 1. It indicates that the rate of AgCl formation and the dissolution of AgCl was not the same [23]. It is inseparable from the characteristic of AgCl, which is a low solubility crystal in the aqueous system [2, 24, 25].

Chloride Sensor Response

Then, after the Ag/AgCl electrode preparation process with varied scan rates and using a 0.1 M KCl solution, it was followed by testing the response to the Cl⁻ ion of each SPE Ag/AgCl at concentration variations of 0.1 – 10⁻⁸ M solution containing Cl⁻ ions or in this case it was the KCl solution. The results of each Ag/AgCl electrode are presented in Table 2 and Figure 5. Based on Table 2 and Figure 5, the scan rate used during the preparation process with the CV technique affected the performance of the resulting Cl ion sensor. Figure 5 shows that at a concentration of 0.1 to 10⁻⁴ M, the resulting potential values were robust and appear to coincide for each Ag/AgCl of SPE. However, at the concentration of < 10⁻⁴ M, the resulting potential value became non-uniform. Besides, based on the data presented in Table 2, the linear range and the longest LOD were at the scan rate of 60 mV/s. It is inseparable from the thickness of the AgCl layer formed on the Ag surface, which is not uniform for each SPE electrode produced so that the sensitivity of the Cl ion sensor varied [2, 16, 23].

Table 2. The performance of the SPE Ag/AgCl chloride ion sensor on varied concentration levels of chloride ions

Scan Rate (mV/s)	Slope (mV/dec)	Linear Range (M)	LOD (M)	r ²
20	-58.6	0.1-10 ⁻⁵	<10 ⁻⁵	0.9877
40	-63.1	0.1-10 ⁻⁵	<10 ⁻⁵	0.9866
60	-53.4	0.1-10 ⁻⁶	<10 ⁻⁶	0.9511
80	-62.0	0.1-10 ⁻⁵	-7.94×10^{-6}	0.9794
100	-68.2	0.1-10 ⁻⁴	-4.79×10^{-5}	0.9983

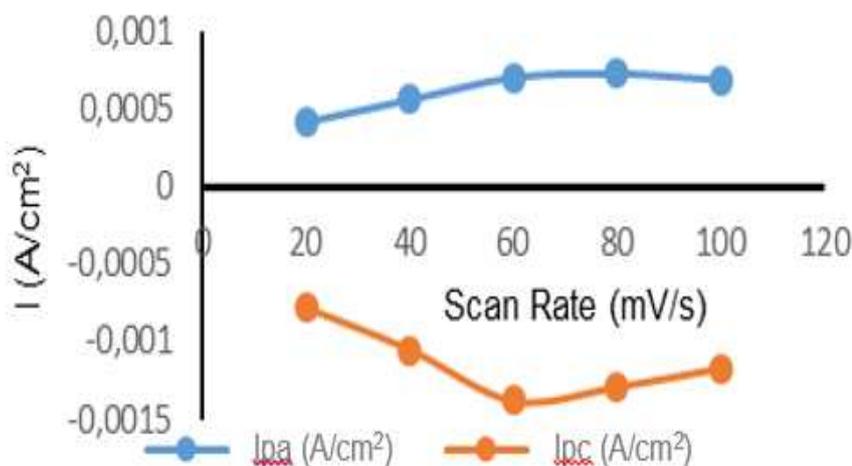


Figure 4. Graph of I_{pa} and I_{pc} coating process of AgCl on the SPE Ag surface at 0.1M KCl solution with varied scan rates for one cycle

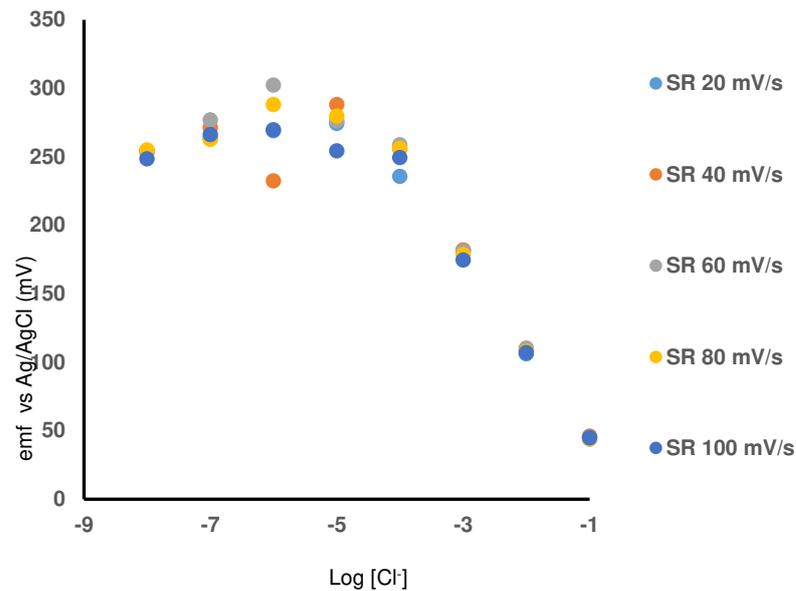
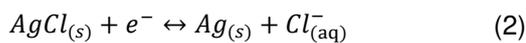


Figure 5. The response of SPE Ag/AgCl on varied concentration levels of chloride ions

At scan rates of 20 and 40 mV/s, the AgCl layer formed did not completely cover the area of the Ag electrode. Thus, it caused some Cl⁻ ions to interact with the Ag surface, and it contributes to the disturbing response of the Cl⁻ ion sensor. Meanwhile, at scan rates of 80 and 100 mV/s, the linear range and LOD values were shorter than the 60 mV/s treatment. In addition, it is affected by the thickness of the AgCl layer, which is thicker and denser as AgCl tends to be an insulator. Therefore, it causes the surface resistivity of the SPE Ag/AgCl to increase, and it contributes to a decrease in sensor sensitivity [16, 22, 23].

The surface of the Ag/AgCl was found to have a fairly good sensitivity to the presence of Cl⁻ ions, where the presence of Cl⁻ ions caused a change in the potential value on the surface of the Ag/AgCl electrode. The potential change followed the AgCl equilibrium equation in the aqueous system following the reaction:



Based on the principle of Le Chatelier that equilibrium will occur in the concentration of products and reactants in the same state, thus (2) can be correlated with the Nernst equation as follows:

$$E = E^0 - \frac{2.303RT}{nF} \text{Log} \frac{[a_{\text{product}}]}{[a_{\text{reactant}}]} \quad (3)$$

Based on (2), the product was Ag and Cl⁻, while AgCl served as the reactant. So, (3) can be determined to (4):

$$E = E^0 - \frac{2.303RT}{nF} \text{Log} \frac{[a_{\text{Ag}}][a_{\text{Cl}^-}]}{[a_{\text{AgCl}}]} \quad (4)$$

Naturally, one of the characteristics of AgCl crystals is the low solubility in the aqueous system, and only a small part of the Cl⁻ ions is released in the aqueous system. Thus, in its equilibrium, the solid AgCl crystals are still present in the aqueous system. Therefore, (4) can be determined to the following equation:

$$E = E^0 - \frac{2.303RT}{nF} \text{Log} \frac{[a_{\text{AgCl}}][a_{\text{Cl}^-}]}{[a_{\text{AgCl}}]} \quad (5)$$

Then, (5) can be simplified into (6):

$$E = E^0 - \frac{2.303RT}{nF} \text{Log} \frac{[\text{Cl}^-]}{[k]} \quad (6)$$

Based on the Nernst equation, R is the ideal gas constant with a value of 8.314 J/K mol, while F is a Faraday number of 96.485 C/mol, n = 1 and at a temperature of 298 K, so that (6) can be determined into:

$$E = E^0 - 59.16\text{mV} \text{Log}[\text{Cl}^-] + 59.16\text{mV} \text{Log}[k] \quad (7)$$

As the value of k is constant, the resulting potential value depends on the change in ion concentration [Cl⁻]. Therefore, (7) can be simplified into (8) [24][25]:

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

Based on (8), the ideal value of the Nernst number for every ten times changes in the concentration of Cl⁻ ions is equivalent to -59.16 mV. In this current research, the optimum Cl⁻ ion sensor response was obtained in preparation at a scan rate of 60 mV / s, with the Nernst number of -53.4 mV/dec and linear ranges between 0.1-10⁻⁶ M. Meanwhile, the LOD value obtained was <10⁻⁶ M with r² value of 0.9511 and it is acceptable referring to Wu et.al that the acceptable r² value for potentiometric measurements reaches > 0.91 [26]. The value of the Nerst number obtained at a scan rate of 60 mV/s is in accordance with the standard Nernst number for monovalent ions of (50) – (-60) mV/dec.

Selectivity Test (Log K^{Pot}_{a,b})

Based on the Cl response test results, three SPE Ag/AgCl were prepared at a scan rate of 60 mV/s as the optimum sensor for the selectivity coefficient test. The selectivity coefficient is one of the parameters to be carried out in fabricating ion-selective electrode (ISE) sensors. This study aims to ensure the ability of the sensor's sensitivity to the presence of other ions that have the potential for reading interference [2, 13, 27].

In general, there are two methods for the selectivity test recommended by the IUPAC, namely the separated solution method (SSM) [2, 13, 28] and the mixed solution method (MSM) [28]. This study used the SSM method as it is simpler, faster, and cheaper than the MSM method [2]. The concept of the SSM method is to compare the potential value of the main ion with the potential value of the interfering ion at the same concentration level of 0.1 M or the highest concentration [28][29]. Moreover, the potential value of the main ion and the interfering ion was based on the following equation:

$$\text{Log} K_{a,b}^{\text{pot}} = \frac{(E_B - E_A)Z_A F}{2.303RT} + \left(1 - \frac{Z_A}{Z_B}\right) \text{Log}[a_A] \quad (9)$$

E_B and E_A are the potential values obtained during the measurement of the interfering ion and the main ion. While Z_A is the main ion load and Z_B is the interfering ion load. Meanwhile, a_A is the activity or concentration in the Molar units of the main ion used in the test [13, 28, 29].

In this study, the interfering ions used included a solution of NO₃⁻, H₂PO₄⁻, HPO₄²⁻, SO₄²⁻ and CO₃²⁻ at a concentration of 0.1 M. The selection of the five types of the interfering ions was based on their potential presence in urine and stinky water samples used in the validation testing [30, 31, 32, 33, 34]. The results of the selectivity coefficient test are presented in Table 3.

Table 3. The value of Log K^{Pot}_{a,b} of the chloride ion sensor on the presence of some types of interfering ions (n=3)

Interfering Ions	Log K ^{Pot} _{a,b}
NO ₃ ⁻	-1.64 ± 0.06
H ₂ PO ₄ ⁻	-3.45 ± 0.03
HPO ₄ ²⁻	-3.74 ± 0.05
SO ₄ ²⁻	-3.93 ± 0.06
CO ₃ ²⁻	-2.34 ± 0.07

Based on the data presented in Table 3, the highest interfering ion is NO₃⁻ ions with a ratio of 1:10. It means that the presence of NO₃⁻ ions in the sample can cause serious interference if it is ten times higher than the chloride ion concentration. Meanwhile, the second-highest interfering comes from the CO₃²⁻ ion with a ratio of 1:100, meaning that it can cause interference if it is 100 times higher than the chloride ion concentration. Furthermore, H₂PO₄⁻ and HPO₄²⁻ could cause serious interference if they are 1000 times higher than chloride ions. Furthermore, the weakest interfering ion is SO₄²⁻ which is close to 1: 10000. It indicates that the risk of interference from other ions can occur if the chloride ion concentration in the sample is low and moderate. Meanwhile, interference caused by other ions is less likely to occur [2].

Lifetime

This lifetime test was to identify how many times the sensor can be used [2]. This study provided one unit of SPE Ag/AgCl electrode and the measurement was at the variation of the concentration of Cl ions between 0.1 – 10⁻⁸ M in which the testing process was stopped if the Nernst number was outside of (-60) - (-50) mV/decade as the standard Nernst number for monovalent anions [2, 16, 27]. The results of the test can be seen in Figure 6.

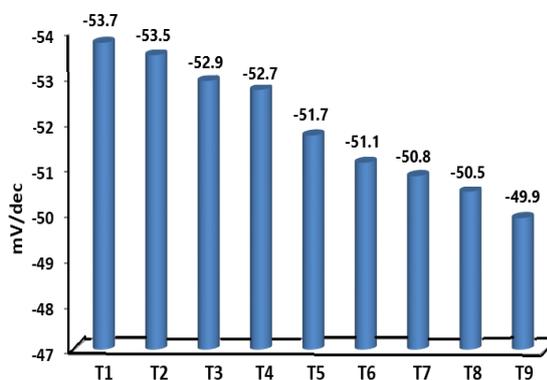


Figure 6. Graph of the Nernst number of the SPE Ag/AgCl chloride ion sensor with some measurements using 0.1 – 10⁻⁸ chloride ion solution

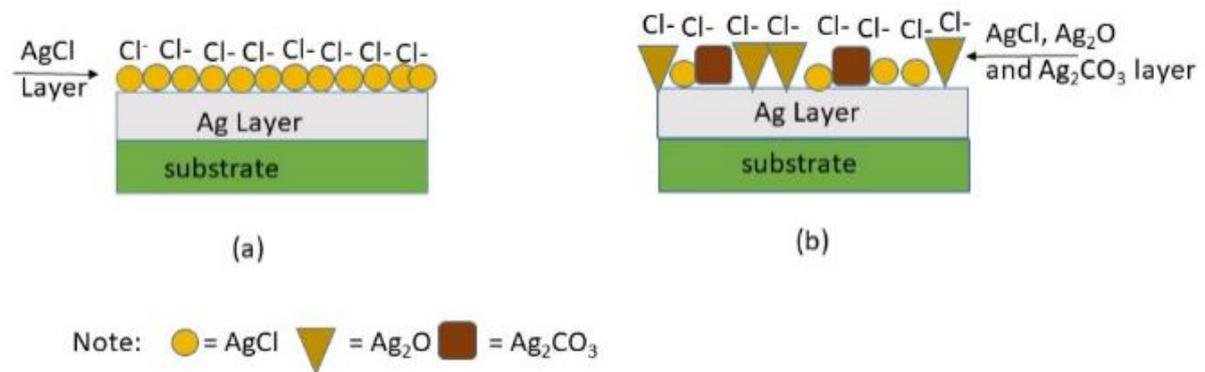
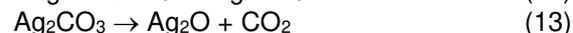


Figure 7. Illustrative images (a) the interaction of chloride ions on the sensor surface in initial use, (b) the interaction of chloride ions on the sensor surface after several uses

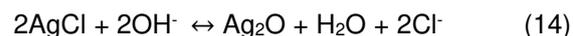
Based on Figure 6, the Nernst number of the Cl Ag/AgCl SPE ion sensor decreased in which in the ninth measurement (T9), which produced a Nernst number of -49.9. It indicates that in the T9 measurement, the obtained Nernst number is out of the standard Nernst number for monovalent anions. Therefore, the prepared Cl SPE Ag/AgCl ion sensor can be used for eight measurements.

The trend of the decrease Nernst number of the Cl SPE Ag/AgCl ion sensor is due to the degradation of the AgCl layer due to the layer formation of Ag₂O and Ag₂CO₃. The formation of a new layer on the surface causes Cl ions from the sample solution to interact with the AgCl surface on the SPE Ag/AgCl electrode, as shown in Figure 7.

The formation of Ag₂O or Ag₂CO₃ layers can occur through slowly dissolving AgCl into the sample and followed by dissolving CO₂ in the sample to form H₂CO₃ as the following reaction mechanism [2][25]:



Besides dissolving CO₂ into the sample solution, the formation of Ag₂O can also go through the reaction process with OH⁻ with the following mechanism [11][35]:



Besides caused by the formation of a new layer on the surface of the Cl ion sensor, a decrease in the response or sensitivity of the Cl ion sensor might be caused by the decomposition of the AgCl layer due to exposure to light. Crystals from the AgX group, including AgCl, are very sensitive to light. Meanwhile, during the testing process, it used a bright testing room and

chamber. Indeed, it increases the potential for light exposure on the SPE Ag/AgCl surface and causes degradation on the sensor surface over time, resulting in decreased sensitivity [36][37].

Validation Test

In the fabrication of a sensor, including the Cl ion sensor, the validation test is necessary. It was to ensure that the performance of the fabricated sensor has the same capabilities as standard methods or using existing equipment [2][27]. In this study, the validation process was by comparing the data from the Cl SPE Ag/AgCl ion sensor results at a scan rate of 60 mV/s with the Ag/AgCl commercial test results. Meanwhile, the samples tested were fresh urine and stinky water. The use of fresh samples was to reduce changes in composition due to microbiological activity and contamination with other materials. Urine and stinky water samples were selected because chloride ions are widely found in urine and stinky water, especially from water treatments [32][38].

The number of sensors used was one sensor for each sample measurement with a certain repetition. The results of the measurement of Cl ions in the sample are presented in Table 4.

Table 4. Comparison of the Cl ions concentration between SPE Ag/AgCl and Ag/AgCl commercial in urine and stinky water samples (n = 3)

Sample	SPE Ag/AgCl (mg/L)	Ag/AgCl Comm (mg/L)
Urine	29.8 ± 1.0	29.9 ± 1.3
Stinky Water	79.3 ± 2.0	79.8 ± 0.2

Based on the data presented in Table 4, the Cl⁻ ion test results in the two samples are not much different. Therefore, it indicates that the SPE Ag/AgCl ion sensor has similar performances to the Ag/AgCl commercial. Thus, it indicates that there is no interference from other ions. Furthermore, the concentration of Cl ions in urine

is in the range of 29 mg/L, and it is still in accordance with health standards of Cl ions in the urine of 25-40 mg/L [39]. Meanwhile, the concentration of Cl ions in stinky water does not exceed 250 mg/L [38].

CONCLUSION

This study reveals that the performance results of the fabrication of the Ag/AgCl electrode can be affected by the scan rate. Based on the obtained data, the optimum Cl⁻ ion sensor response was at a scan rate of 60 mV/s with the value of the Nernst number of -53.4 mV/dec and a linear range of 0.1-10⁻⁶ M. The NO₃⁻ ion gives the strongest interference followed by CO₃²⁻, H₂PO₄⁻, HPO₄²⁻ respectively and the weakest is SO₄²⁻. The Cl SPE Ag/AgCl ion sensor prepared can be used for at least eight measurements in the lifetime test. Then, the validation test results show that the Cl ions in the two samples are not much different. It indicates that the SPE Ag/AgCl ion sensor has a similar performance with the Ag/AgCl commercial.

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REFERENCES

- [1] A. Mahmoudi., S. Shakibania., S. Rezaee, M. Mokmeli, "Effect of the chloride content of seawater on the copper solvent extraction using Acorga M5774 and LIX 984N extractants," *Separation and Purification Technology*, volume 251, pp: 117394, 2020, doi: 10.1016/j.seppur.2020.117394
- [2] S. Alva, E. Hindasah, W. A. W. Jamil, and 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
- [3] E. Tatjana, H. Neidhardt, N. Pagano, M. A. W. Marks, G. Mark, and Y. Oelmann, "Vegetation canopy effects on total and dissolved Cl, Br, F and I concentrations in soil and their fate along the hydrological flow path," *Science of The Total Environment*, vol. 712, pp: 135473, 2020, doi: 10.1016/j.scitotenv.2019.135473
- [4] M. Li, T. Zhou, M. Zu, S. Zhang, Y. Liu, and H. Zhao, "Membrane-based colorimetric flow-injection system for online free chlorine monitoring in drinking water," *Sensors and Actuators B: Chemical*, vol. 327, pp: 128905, 2021, doi: 10.1016/j.snb.2020.128905
- [5] K. Nakata, T. Hasegawa, T. Higashihara, T. Oyama, "Chloride ion concentrations during the compression of rocks to extract pore water," *Geofluids*, vol. 16, pp: 78-88, 2016, doi: 10.1111/gfl.12137
- [6] H. S. El-Sheshtawy and I. El-Mehasseb, "Role of halogen and hydrogen bonds for stabilization of antithyroid drugs with hypohalous acids (HOX, X = I, Br, and Cl) adducts," *Journal of Molecular Structure*, vol. 1147, pp: 643-650, 2017, doi: 10.1016/j.molstruc.2017.06.141
- [7] B. Agirman and H. Erten, "The Influence of Various Chloride Salts to Reduce Sodium Content on the Quality Parameters of Şalgam (Shalgam): A Traditional Turkish Beverage Based on Black Carrot", *Journal of Food Quality*, vol. 2018, Article ID 3292185, 2018, doi: 10.1155/2018/3292185
- [8] M. Park, I. P. Jeon, J. Ryu, H. Jang, J. B. Back, and J. Cho, (2016), "Edge-halogenated graphene nanoplatelets with F, Cl, or Br as electrocatalysts for all-vanadium redox flow batteries," *Nano Energy*, Volume 26, pp: 233-240, 2016, doi: 10.1016/j.nanoen.2016.05.027
- [9] C. Amsaraj, R. Bharathikannan, P. Muthurajab, and M. Rajkumar, "Chlorine directed C-Cl ... π and C-H...Cl interactions in acridinium 3,5-dichlorosalicylate: Synthesis, X-ray diffraction and theoretical analysis," *Journal of Molecular Structure*, vol. 1220, pp: 128759, 2020, doi: 10.1016/j.molstruc.2020.128759
- [10] A. Cranny, N. Harris, N. White, "Screen Printed Potentiometric Chloride Sensors," *Procedia Engineering*, vol. 87, pp: 220 - 223, 2014, doi: 10.1016/j.proeng.2014.11.626
- [11] F. Pargar, D. A. Koleva, and K. Breugel, "Determination of Chloride Content in Cementitious Materials: From Fundamental Aspects to Application of Ag/AgCl Chloride Sensors," *Sensors*, vol. 17, no. 2482, pp: 1-22, 2017, doi:10.3390/s17112482
- [12] P. Jat and M. L. Serre, "Bayesian Maximum Entropy space/time estimation of surface water chloride in Maryland using river distances," *Environmental Pollution*, vol. 219, pp: 1148-1155, 2016, doi: 10.1016/j.envpol.2016.09.020
- [13] 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," *Journal of The Electrochemical Society*, vol. 166, no. 15, pp.

- B1513-B1519, 2019, doi: 10.1149/2.0601915jes
- [14] Y. Abbas, X. Zhua, H. L. Boer, N. B. Tanvir, W. Olthuis, and A. Berg, "Potentiometric measurement with a Kelvin probe: Contactless measurement of chloride ions in aqueous electrolyte", *Sensors and Actuators B: Chemical*, vol. 236, pp: 1126-1132, 2016, doi: 10.1016/j.snb.2016.06.150
- [15] R. T. Maminska, M. Kloch, A. Z. Deniziak, and A. Bala, "Design and characterization of novel all-solid-state potentiometric sensor array dedicated to physiological measurements," *Talanta*, vol. 159, pp: 7-13, 2016, doi: 10.1016/j.talanta.2016.06.001
- [16] D. S. Khaerudini, F. Rahman, and S. Alva, "Optimization strategy of Ag/AgCl thin film electrodes approached by chlorination process for electrochemical response materials," *Materials Chemistry and Physics*, vol. 240, pp: 122294, 2020, doi: 10.1016/j.matchemphys.2019.122294
- [17] P. J. Brewer, R. J. Leese, R. J. C. Brown, "An improved approach for fabricating Ag/AgCl reference electrodes," *Electrochimica Acta*, vol. 71, pp. 252-257, 2012, doi:10.1016/j.electacta.2012.03.164
- [18] L. Fu, A. Wang, Y. Zheng, W. Cai, Z. Zhuxian Fu, "Electrodeposition of Ag dendrites/AgCl hybrid film as a novel photodetector," *Materials Letters*, vol. 142, pp:119-121, 2015, doi: 10.1016/j.matlet.2014. 12.001
- [19] I. Hanafi, A. R. Daud, S. Radiman, "Cyclic Voltammetric Study of Co-Ni-Fe Alloys Electrodeposition in Sulfate Medium," *AIP Conf. Proc.*, vol. 1571, pp: 120-124, 2014, doi: 10.1063/1.4858640
- [20] Y. Kim, J. Jung, S. Kim, and W. S. Chae, "Cyclic Voltammetric and Chronoamperometric Deposition of CdS", *Materials Transactions*, vol. 54, no. 8, pp. 1467-472, 2013, doi: 10.2320/matertrans. M2013125
- [21] H. M. A. Amin, Y. Uchida, C. B. McAuley, E. Katelhon, and R. G. Compton, R.G., "Non-triangular potential sweep cyclic voltammetry of reversible electron transfer: Experiment meets theory," *Journal of Electroanalytical Chemistry*, vol. 815, pp: 24-29, 2018. doi: 10.1016/j.jelechem.2018.03.001
- [22] X. Jin, J. Lu, P. Liu, and H. Tong, "The electrochemical formation and reduction of a thick AgCl deposition layer on a silver substrate," *Journal of Electroanalytical Chemistry*, vol. 542, pp: 85-96, 2003, doi: 10.1016/S0022-0728(02)01474-2
- [23] E. M. Espinoza, J. A. Clark, J. Soliman, J. B. Derr, M. Morales, and V. I. Vullev, "Practical Aspects of Cyclic Voltammetry: How to Estimate Reduction Potentials When Irreversibility Prevails," *Journal of The Electrochemical Society*, vol. 166, no. 5, pp: H3175-H3187, 2019, doi: 10.1149/2.0241905jes
- [24] A. Cranny, N. R. Harris, M. Nie, J. A. Wharton, R. J. K. Wood, and K. R. Stokes, "Screen-printed potentiometric Ag/AgCl chloride sensors: Lifetime performance and their use in soil salt measurements," *Sensors and Actuators A: Physical*, vol. 169, no. 2, pp: 288-294, 2019, doi: 10.1016/j.sna.2011.01. 016
- [25] S. Alva, A. S. A. Aziz, M. I. Syono, and W. A. W. Jamil, "Ag/AgCl Reference Electrode Based on Thin Film of Arabic Gum Membrane," *Indonesian Journal of Chemistry*, vol. 18, no. 3, pp: 479-485, 2018, doi: 10.22146/ijc.28859
- [26] R. Wu, X. G. Chen, C. Tao, Y. Huang, Y. Ye, Q. Wang, Y. Zhou, Q. Jin, and W. Cai, "An All-Solid-State Silicate Ion-Selective Electrode Using PbSiO₃ as a Sensitive Membrane," *Sensors*, vol. 19, no. 5, pp: 1-7, 2019, doi: 10.3390/s19030525
- [27] S. Alva, R. Suherman, F. Friliandita, 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," *Indonesian Journal of Chemistry*, vol. 20, no. 3, pp: 645-654, 2020, doi: 10.22146/ijc.44478
- [28] Y. Umezawa et al., "Potentiometric Selectivity Coefficients of Ion-Selective Electrodes: Part 1. Inorganic Cations," *Pure and Applied Chemistry*, vol. 72, no. 10, pp. 1851-2082, 2000, doi: 10.1351/pac200072101851
- [29] E. Luboch, M. Jeszke, M. Szarmach, and N. Lukasik, "New bis (azobenzocrown)s with dodecylmethylmalonyl linkers as ionophores for sodium selective potentiometric sensors," *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, vol. 86, pp: 323-335, 2016, doi: 10.1007/s10847-016-0661-9
- [30] I. Yaroshenko, D. Kirsanov, L. Kartsova, A. Sidorova, I. Borisova, and A. Legin, "Determination of urine ionic composition with potentiometric multisensor system", *Talanta*, vol. 131, pp: 556-561, 2015, doi: 10.1016/j.talanta. 2014.08.030
- [31] K. S. Kamel, S. C. Dhadli, and M. L. Halperin, "Studies on the pathophysiology of the low urine pH in patients with uric acid stones," *Kidney International*, vo. 61, no. 3, pp. 988-994, 2002, doi: 10.1046/j.1523-1755.2002. 00197.x

- [32] B. Saad, F. W. Pok, A. N. A. Sujari, and M. I. Saleh, "Analysis of anions and cations in drinking water samples by Capillary Ion Analysis," *Food Chemistry*, vol. 61, no. 1/2, pp. 249-254, 1998, doi: 10.1016/S0308-8146(97)00024-1
- [33] J. Liu, Y. Li, J. Jiang, X. Zhang, V. K. Sharma and C. M. Sayes, "Effects of ascorbate and carbonate on the conversion and developmental toxicity of halogenated disinfection byproducts during boiling of tap water," *Chemosphere*, vol. 254, pp: 126890, 2020, doi: 10.1016/j.chemosphere.2020.126890
- [34] R. N. Bian, X. Xu, T. Feng, and W. K. Dong, "A novel O-phenanthroline-based bis(half-salamo)-like chemical sensor: For rapid and efficient continuous recognition of Cu^{2+} , HPO_4^{2-} and H_2PO_4^- ," *Inorganica Chimica Acta*, vol. 516, ID: 120098, 2021, doi: 10.1016/j.ica.2020.120098
- [35] Y. S. Femenias, U. Angst, F. Caruso, and B. Elsener, "Ag/AgCl ion-selective electrodes in neutral and alkaline environments containing interfering ions," *Materials and Structures*, vol. 49, pp: 2637-2651, 2016, doi: 10.1617/s11527-015-0673-8
- [36] C. Han, L. Ge, C. Chen, Y. Li, Z. Zhao, X. Xiao, Z. Li, and J. Zhan, "Site-selected synthesis of novel Ag@AgCl nanoframes with efficient visible light induced photocatalytic activity," *Journal of Materials Chemistry A*, vol. 2, pp: 12594-12600, 2014, doi: 10.1039/C4TA01941E
- [37] X. Wanga, J. Yua, C. Fua, T. Lia, H. Yu, "Self-templated formation of AgCl/TiO₂ hollow octahedra for improved visible-light photocatalytic activity," *Applied Surface Science*, vol. 494, pp: 740-748, 2019, doi: 10.1016/j.apsusc.2019.07.221
- [38] D. L. Rocha and F. R. P. Rocha, "An environmentally friendly flow-based procedure with photo-induced oxidation for the spectrophotometric determination of chloride in urine and waters," *Microchemical Journal*, vol. 108, pp:193-198, 2013, doi: 10.1016/j.microc.2012.10.020
- [39] P. M. Villeneuve and S. M. Bagshaw, "Assessment of Urine Biochemistry," in *Critical Care Nephrology*, 3rd Ed., pp. 323-328.e1, Editors: C. Ronco, R. Bellomo, J. Kellum, Z. Ricci, Elsevier,UK, 2019, doi: 10.1016/B978-0-323-44942-7.00055-8