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## Effect of Conductive Coating on Silver/Silver Chloride Electrodes for Cathodic Protection Application

Karyanto Herlambang<sup>1\*</sup>, Pradipta Dwi Briyantama<sup>2</sup>

<sup>1</sup>Metallurgy Study Program, Institute Technology Science Bandung, Bandung, Indonesia

<sup>2</sup>PT PGAS Solution Subsidiary of Pertamina Gas Negara, Jakarta, Indonesia

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#### \*Corresponding author:

Karyanto Herlambang

#### E-mail address:

[kherlambang@itsb.ac.id](mailto:kherlambang@itsb.ac.id)

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### ABSTRACT

Measurement of pipe to soil potential in a cathodic protection system is something that must be done which aims to monitor the performance of the installed cathodic protection system. The main measuring tool in measuring pipe to soil potential is the reference electrode. The stability of the reference electrode is important as a validation of the measurement results. So far, the stability of the reference electrode is very difficult to maintain due to frequent changes caused by the environment, especially for permanent reference electrodes that are buried in the underground or installed in seawater. Permanent reference electrode sensors commonly used in seawater is the Ag/AgCl reference electrode, but in fact the Ag/AgCl reference electrode is generally unstable and must be stabilized with a KCl solution and other problems have not been produced in Indonesia. This research will be carried out by adding a conductive layer to the Ag/AgCl electrode so that its stability can be increased. The sensor manufacturing process starts from pretreatment, electrolysis and product characterization. The results of the best coating thickness and weight gain experiments showed by the highest voltage variations and time variations (4000mV and 60 minutes). The presence of conductive solid material increases corrosion resistance from 0.00391 mm/year to 0.19549 mm/year and increases the stability of the Ag/AgCl layer  $\pm 5$  mV.

### 1. Introduction

Advances in information technology are always developing, where development of information technology is now starting to penetrate into various areas of life, and it cannot be denied that information technology can increase effectiveness and efficiency in a job. One area that follows the progress of information technology is the field of cathodic protection. One of the roles of information technology in this field is known as online cathodic protection monitoring technology, so advances in information technology will make online cathodic protection monitoring technology more developed.<sup>1-3</sup>

The cathodic protection online monitoring system is a system that aims to monitor and control the pipe

to soil potential from pipes in a place without pipe surveyors coming to the field.<sup>4</sup> The development of cathodic protection online monitoring technology depends on the network system and cathodic protection system. In cathodic protection online monitoring technology, the cathodic protection system used is a structure that is protected by a cathodic protection sensor (permanent reference electrode) that is buried in the underground.<sup>5,6</sup> The cathodic protection online monitoring system will provide accurate data if the permanent reference electrode sensor is embedded in a stable environment over time. Unstable or easily corroded permanent electrodes will provide inaccurate measurement data.<sup>7,8</sup>

One type of permanent reference electrode sensor commonly used in seawater is the Ag/AgCl reference electrode. Its main function is to measure the potential value (protection) of the cathodic protection given to structures in seawater. The Ag/AgCl reference electrode used to measure the degree of structural protection is generally unstable and must be stabilized with a KCl solution. The process of Ag/AgCl instability is caused by the environment of the electrode, which can cause corrosion on the AgCl layer besides that, the instability of the AgCl layer on the Ag/AgCl electrode.<sup>8-11</sup> The study aimed to make a permanent Ag/AgCl reference electrode and utilize solid polymer media as an Ag/AgCl environment so that the stability of the reference electrode can be maintained.

## 2. Methods

### Tools and materials

The equipment used in this research were Mettler AE200 digital scales, SANFIX SP-305E power supply, optical microscope, heater, 100 ml measuring cup, 250 ml beaker glass, petri dish, mounting block, multimeter SANWA PC700, thermometer, grinding machine and potentiostat. The materials used in this research were KCl powder, water, silver wire, platinum wire, conductive polymer, resin and catalyst, cooper wire, seawater, and sandpaper grade 1000 to 5000.

### Research procedure

This research procedure begins with making an AgCl layer on the silver wire, and then the results will be compared if using a conductive layer with one that does not use a conductive layer. Diagrammatically, the research procedure can be seen in Figure 1.

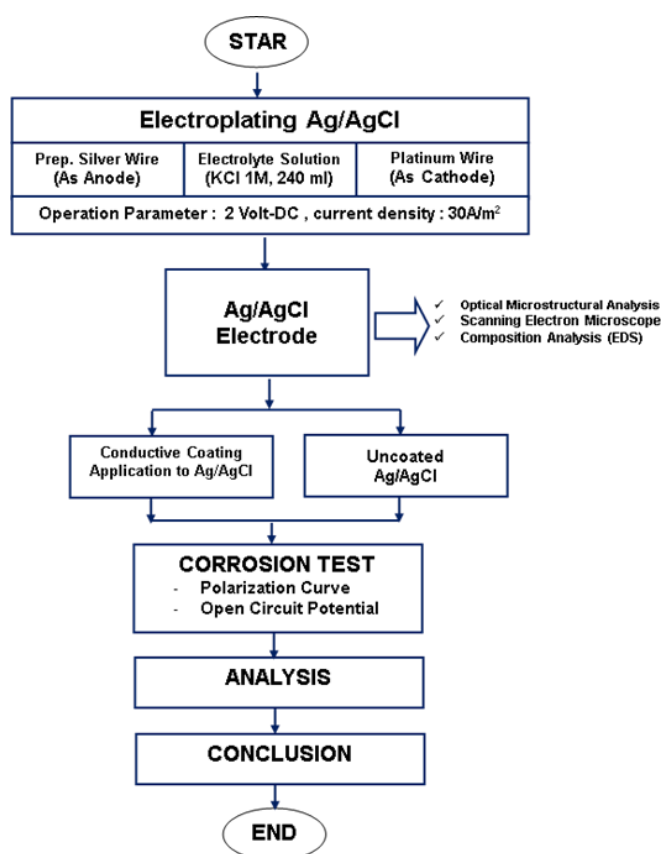


Figure 1. Research procedure.

Silver wire was cut with a length 5 cm and then pretreated with distilled water, soapy water, and lime juice. These silver wire ends are connected with copper wire that has been formed in such a way. 250 ml of 1M KCl solution was prepared. The power supply is connected to the ends of the poles with cables whose ends have been given alligator clamps. Silver and

platinum wires were connected to each pole of the power supply and then dipped into 1M KCl solution with time variations of 15, 30, 45, and 60 minutes and voltage variations of 1000, 2000, 3000, and 4000 mV. The wire is removed and dried, the AgCl will stick to the silver wire, and then the silver wire will be black-gray

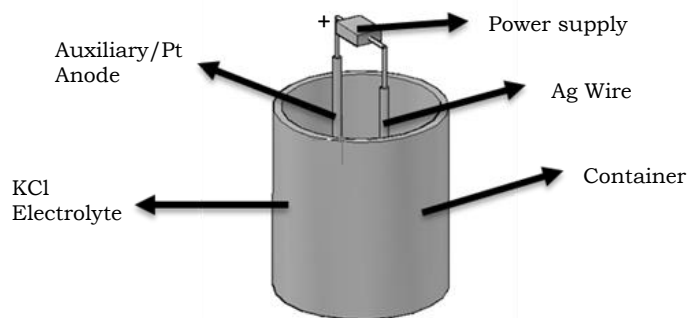


Figure 2. AgCl mechanism process.<sup>12</sup>

### Microstructural analysis

Microstructural analysis was carried out by metallographic method according to ASTM E3-11 standard. In this test, etching was carried out with a solution according to the ASTM 20 standard, then the results of the microstructural picture were taken, then compared with the literature and analyzed.

### Coating thickness analysis

Coating thickness analysis was carried out by visual inspection using an optical microscope.

### Weight Analysis

Analysis of weight was carried out by weighing the difference in the initial weight of Ag before and after going through the electroplating process using an AE200 digital scale.

### SEM & EDX analysis

SEM & EDX analysis was performed using a JEOL SEM instrument (JED-2200 Series). The test sample is placed on the aluminum holder using glue adhesive. The sample is put into a vacuum chamber, while electrons are generated from the filament and then accelerated so that they hit the sample. The results of

the SEM and EDX images can then be analyzed.

### Polarization analysis

Polarization test analysis was carried out by Gamry reference 600 potentiostat instrument equipped with an application Gamry framework. The potentiodynamic test was carried out at -0.25 V to 0.25 V for corrosion potential (vs. Eoc). The scan rate used is 0.167 mV/s according to the ASTM G5 standard. The polarization test was carried out on two samples, namely the Ag/AgCl sample coated and uncoated by a conductive solid material with the same variation of time and voltage.

### Corrosion potential analysis

Potential testing was carried out using the PC700 Digital Multimeter instrument equipped with the PCLink 7 application on a laptop using a platinum comparator. Potential testing was carried out for 2 weeks and carried out every day for 2 hours. The potential test was carried out on two samples, namely the Ag/AgCl sample coated and uncoated by a conductive solid material with the same variation of time and voltage.

### 3. Results and Discussion

#### Microstructural analysis

Based on Figure 3, it can be analyzed that the grain shape of the specimen and the literature have similarities where the grain shape is not straight and

has a puzzle-like shape (jigsaw) but does not have a 100% similarity due to the different magnification of the images taken, from these observations it can be concluded that the samples taken use is pure silver.

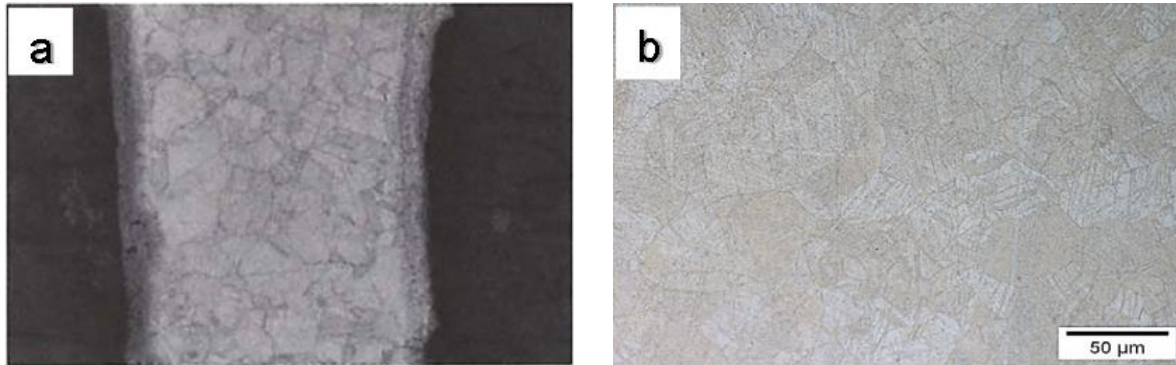


Figure 3. Silver microstructure; (a) literature<sup>13,14</sup>; (b) the results from the study.

#### Coating thickness with various voltage and time analysis

The coating results of the AgCl electroplating process on the Ag substrate can be seen in the microstructural analysis below, where the layer thickness can be graphed, as seen in Figure 4. The

results of measuring the thickness of the AgCl film layer are then graphed, as seen in Figure 5. The thickness results of the AgCl layer with electroplating time can be seen in Figure 6. The results of measuring the thickness of the AgCl film layer are then graphed as in Figure 7.

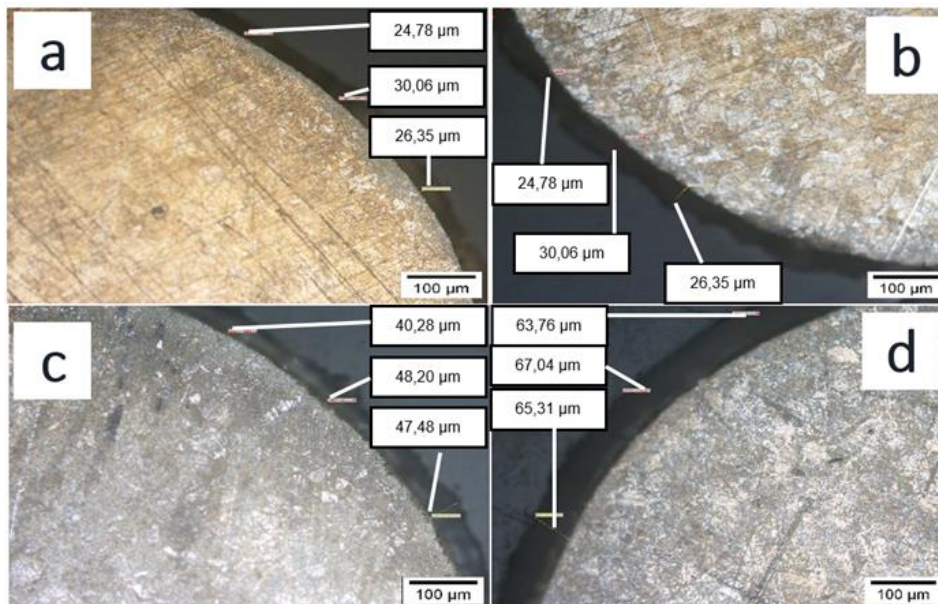


Figure 4. AgCl film microstructure on silver wire substate as a function of voltage; (a) 1000 mVolt; (b) 2000 mVolt; (c) 3000 mVolt; (d) 4000 Volt.

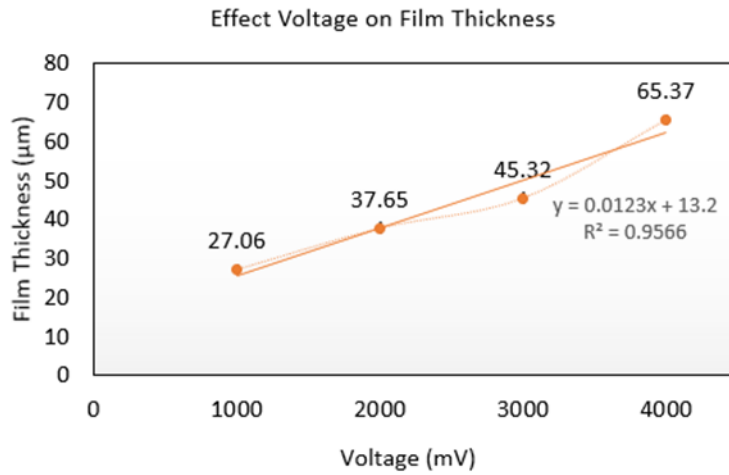


Figure 5. Coating thickness on various voltages.

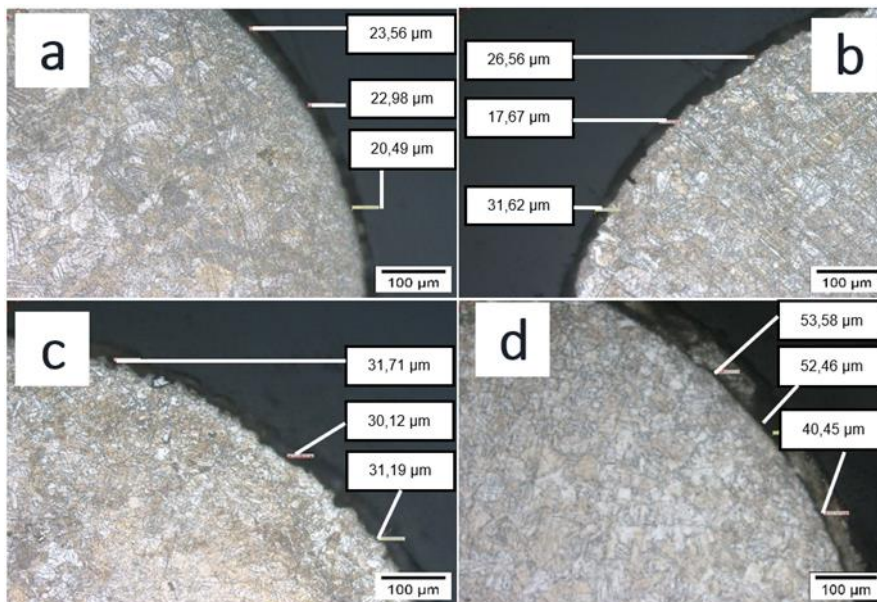


Figure 6. Image of Coating Thickness as a function of electroplating time; (a) 15 minutes; (b) 30 minutes; (c) 45 minutes; (d) 60 minutes.

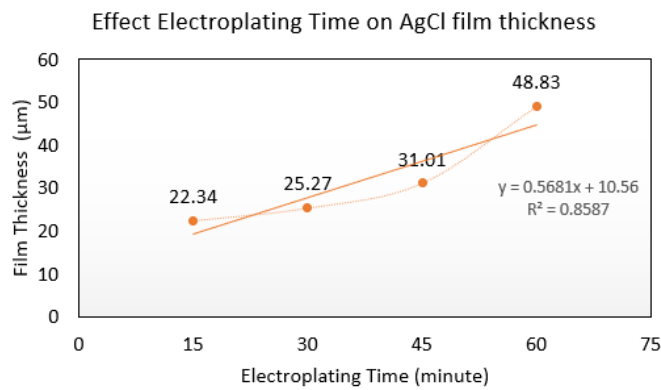


Figure 7. Coating thickness on various electroplating times.

From these data, it can be analyzed that the greater the voltage applied to the specimen, the thickness of the AgCl layer on pure Ag will increase. This is caused by increasing the amount of voltage flowing during the electroplating process. The number of Cl<sup>-</sup> ions will be more released from K<sup>+</sup> so that the amount of Cl<sup>-</sup> released from the solution will precipitate or stick to the workpiece.<sup>10,12</sup> From these data, it can be analyzed that the longer the electroplating process of Ag to Ag/AgCl, the thickness of the AgCl layer on pure Ag will increase. This is because the longer the electroplating process lasts, the portion of the accumulated movement of electrons and material transfer at the two electrodes also increases.

### AgCl film weight with various voltage and time analysis

From Figure 8, it can be analyzed that the greater the voltage, the weight gained on the specimen will increase. This is due to the increasing amount of voltage flowing during the electroplating process. The more Cl<sup>-</sup> ions will be released from K<sup>+</sup> so that a large amount of Cl<sup>-</sup> released from the solution will precipitate or stick to the workpiece. From these data, it can be analyzed that the longer the processing time, the weight gained on the specimen will increase. This is due to the longer the process takes place electroplating, the portion of the accumulation of electron movement and material transfer at the two electrodes will also increase. Cl<sup>-</sup> which binds to Ag<sup>+</sup> and will increase weight gain.

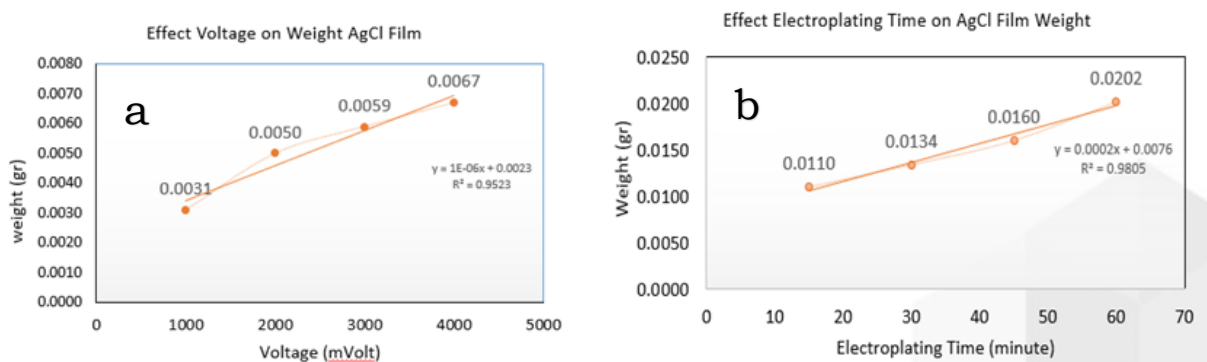


Figure 8. Weight analysis; (a) various voltage; (b) various times.

### SEM & EDX analysis

Figure 9 (a) is a photo of the results of the SEM test taken using 50 X magnification. It can be seen that the flat part is Ag while the lump-shaped part is AgCl. Figure 9 (b) is a photo of the results of the SEM test taken using a magnification of 1000 X in an area of the sample. It is clearer that there is porous AgCl in the Ag metal where the white part is Ag while the black part is Porous AgCl, but not all parts of Ag turn into

AgCl because the voltage is not too high, the processing time and heating time are not too long. The microstructural condition of the porous AgCl layer is one of the reasons why the stability of the Ag/AgCl electrode is unstable when it interacts with the environment. This condition of decreasing stability of the Ag/AgCl electrode can be analytically improved by adding a conductive solid layer.

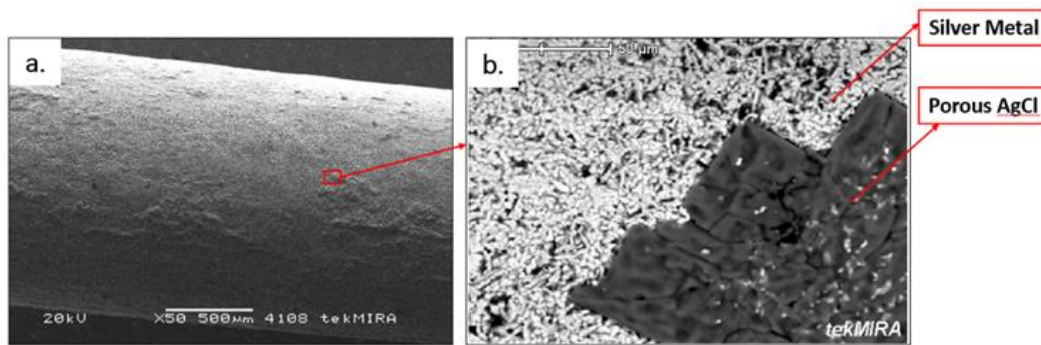


Figure 9. SEM test results for porous AgCl on Ag (a) 50X (b) 1000X.

### Polarization analysis

Polarization analysis was carried out to see the current density and corrosion rate of the AgCl material using and without using a conductive layer. The polarization curve can be seen in Figure 10. Sample A is an Ag/AgCl layer covered with conductive solid material, while sample B is an Ag/AgCl layer without being coated with conductive solid material. The results of the polarization curve show that the corrosion rate of the Ag/AgCl material coated with conductive solid material was 0.00391 mm/year, and

without being coated with conductive solid material was 0.19549 mm/year. From these results, it can be analyzed that the resistance of the Ag/AgCl material coated with conductive solid material has better corrosion resistance compared to that without being coated with conductive solid material. This is because Ag/AgCl without the conductive solid layer does not have any protection and will directly interact with the seawater environment where there is a Cl<sup>-</sup> content, which can cause corrosion.

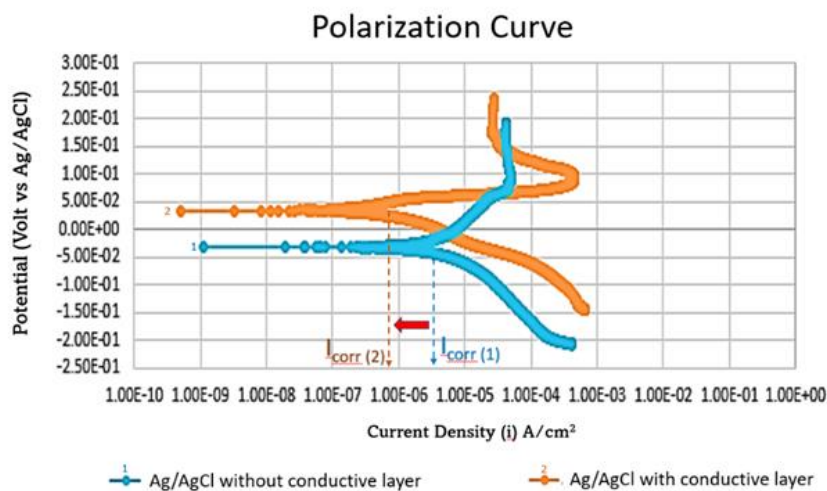


Figure 10. Polarization curve.

### Potential analysis

Potential measurements were carried out using a data logger, which was recorded for up to 500 hours to see the stability of the Ag/AgCl electrode potential (Figure 11). This potential data recording was carried

out for up to 500 hours, and it was seen that the Ag/AgCl electrode coated with a solid conductive material looked more stable than the ordinary Ag/AgCl electrode (Table 1).

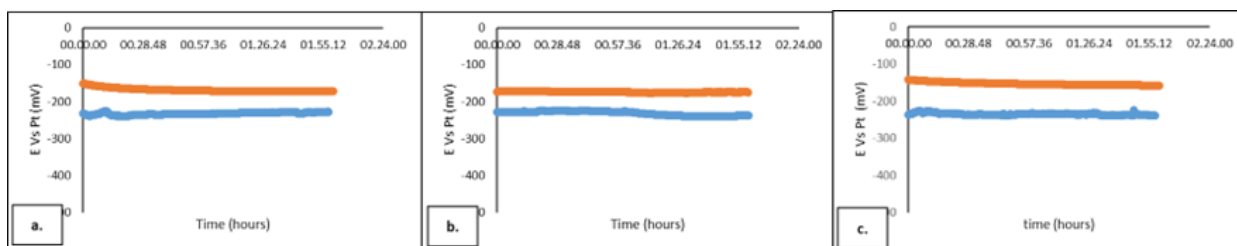


Figure 11. Data logger open circuit potential record Ag/AgCl with and without conductive layer.

Table 1. Open circuit potential record of Ag/AgCl.

No.	Materials	24 hours	48 hours	72 hours	336 hours	500 hours
1	Ag/AgCl without conductive layer (E vs Platinum electrode)	-167,93 mV	-173,86 mV	-153,06 mV	-104,4 mV	-75,1 mV
2	Ag/AgCl with a conductive layer (E vs Platinum electrode)	-232,11 mV	-231,18 mV	-234,84 mV	-234,1 mV	-230,5 mV

This stability is due to the conductive layer being a conductive carbon layer, as was also done by previous researchers.<sup>15-17</sup> In this research, the conductive material applied can also maintain the stability of the Ag/AgCl electrode. The corrosion stability of the Ag/AgCl layer with a layer of conductive solid material has a better level of stability compared to Ag/AgCl without conductive solid material where the stability is still in the range of less than  $\pm 5$  mV, which is the target of the test criteria. So, it can be analyzed that there are conductive solid materials that can increase the stability of Ag/AgCl and Ag/AgCl layers coated with conductive solid materials. Their potential will not change beyond the design life (more than 20 years) and can be used in industrial applications.

#### 4. Conclusion

Comparison electrodes Ag/AgCl for cathodic protection systems can be made by electrolysis methods. The Ag/AgCl reference electrode can be used for cathodic protection online monitoring systems. The corrosion polarization resistance of the Ag/AgCl layer covered with conductive solid material shows a stable corrosion resistance from high to low, which is 0.19549 mm/year to 0.00391 mm/year. Increasing the processing time and stress increases the thickness of AgCl on Ag metal. Scanning electron microscope (SEM) results show the formation of porous AgCl in Ag

metal, and this is what causes the stability of the Ag/AgCl electrode to become more susceptible to the environment. The presence of a conductive layer on AgCl can provide stability to the Ag/AgCl electrode for cathodic protection applications.

#### 5. References

1. Hudson SM, Taylor JT, Bowen CR. Energy harvesting of cathodic protection currents in subsea and marine structures for wireless sensor power and communication. *Appl Energy*. 2022; 316: 119133.
2. Merten BJE. Embedded reference electrodes for corrosion potential monitoring, electrochemical characterization, and controlled-potential cathodic protection. NDSU Repository. 2011.
3. Song D. A real-time non-contact monitoring method of subsea pipelines. *MATEC Web of Conferences*, 2015; 34: 1-4.
4. Al-Attabi A, Hussein M. Remote monitoring of oil pipelines' cathodic protection system via GSM/GPRS modem and the thingspeak platform. *Diagnostyka*. 2022; 23(3): 1-7.
5. Janda D. Cathodic protection - It's all about current, NACE - International Corrosion Conference Series, 2010; 10034: 1-9.
6. Wyatt BS. Reference electrodes for monitoring cathodic protection on buried pipelines pre-



- standard: Ceocor Working Group Publication. in CEECOR External Corrosion and Cathodic Protection, CEECOR Commission 2. 2018; 1–32.
7. Wyatt BS. Reference electrodes for monitoring cathodic protection on buried pipelines pre-standard: Ceocor Working Group Publication. in CEECOR External Corrosion and Cathodic Protection, CEECOR Commission 2. 2018; 1–32.
  8. Dean Jr SW. Electrode potential as a key indicator of corrosion performance. 2019; 1609: 211–30
  9. Huda M. Making Ag/AgCl comparison electrodes using a carbon-rattan composite membrane. Prosiding Skripsi Institut Teknologi Sepuluh Nopember. 2010; 30(8): 92–5.
  10. Kurniawan F. Ag/AgCl comparison electrode fabrication with various membranes. Akta Kimia Indonesia. 2017; 2(1): 70
  11. Kurniawan JF. Electrochemical performance study of Ag/AgCl and Au flexible electrodes for unobtrusive monitoring of human biopotentials,” Nano Select. 2022; 3(8): 1277–87
  12. Darmawan S. The influence variation of strong electric current time and process electroplating power of attraction, violence and layer thickness on low carbon steel with chrome. Dinamika Teknik Mesin. 2015; 5(2): 66–71.
  13. ASM Handbook Volume 2: properties and selection: nonferrous alloys and special-purpose materials, ASM International, 1998; 2(3).
  14. Scott DA. Metallography and microstructure of ancient and historic metals. The J. Paul Getty Trust. 1991.
  15. Li GZ, Feng LJ, Zhai Z, Wang FF. Effect of different carbon materials on the conductivity of epoxy resin conductive coatings. Materials Science Forum, 2021; 1020: 164–9.
  16. Patole A, Lubineau G. Carbon nanotubes with silver nanoparticle decoration and conductive polymer coating for improving the electrical conductivity of polycarbonate composites. Carbon N Y. 2015; 81(1): 720–30.
  17. Nguyen TSV, Huynh TM, To TD, Doan TCD, Dang CM. Ag/AgCl film electrodes coated with agarose gel as planar reference electrodes for potentiometric sensors. Universal Journal of Materials Science. 2018; 6(5): 148–54.