

Performance of Disposable Cu/CuSO₄ Reference Electrode in Reinforced Concrete Corrosion Analysis

(Prestasi Elektrod Rujukan Cu/CuSO₄ Pakai Buang dalam Analisis Kakisan Konkrit Tetulang)

MUHAMMAD IHSAN^{1,2,5}, SYARIZAL FONNA^{2*}, SYIFAUL HUZNI², NURUL ISLAMI,³ SAGIR ALVA⁴ & AHMAD KAMAL ARIFFIN⁵

¹*Faculty of Engineering, Universitas Gajah Putih, 24552, Takengon, Indonesia*

²*Department of Mechanical & Industrial Engineering, Universitas Syiah Kuala, Banda Aceh, Indonesia*

³*Material Engineering, Malikussaleh University, Lhokseumawe, Indonesia*

⁴*Mechanical Engineering Department, Universitas Mercu Buana, West Jakarta, Indonesia*

⁵*Centre for Integrated Design for Advanced Mechanical Systems
Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia*

Received: 23 December 2022/Accepted: 15 August 2023

ABSTRACT

The investigation of reference electrode performance for corrosion analysis has been widely conducted over the last decade. The need for a disposable and reliable reference electrode is a specific need for corrosion investigation. This research investigated the effectiveness of *liquid-based* and *solid-state* reference electrodes, which are disposable and provide reliable performance. The electrode was prepared with low-cost material preparation (disposable usage) within a Copper-Copper Sulphate (CCS) *liquid-based* and *solid-state* electrodes. The potential stability was already tested for dependability by measuring the Open Circuit Potential (OCP) on the rebar concrete specimen. The behaviour of *solid-state* reference and *liquid-based* reference electrodes in terms of polarization was studied in a corroded environment. Real-time potential data was also obtained for the corrosion rate investigation. The result shows the consistency performance of (OCP) value during corrosion measurement. The deviation of the maximum to a minimum potential value less than 0.02 V, verifies that the *liquid-based* copper (Cu) electrode and *solid-state* copper (Cu) electrodes are reliable, adaptable, and disposable for reinforced concrete corrosion measurement. In terms of corroded rebar potential measurement, the real-time polarization measurement result shows that the high-risk corroding occurred on the embedded rebar and was validated by directly visualizing the rebar concrete specimen. Therefore, the results obtained allow us to conclude that the disposable of both reference electrodes shows their stability and significantly reduces the reinforced concrete corrosion research cost.

Keywords: Concrete corrosion; copper-copper sulphate; Cu/CuSO₄; potential analysis; reference electrode

ABSTRAK

Prestasi elektrod rujukan untuk analisis kakisan dikaji secara meluas sejak beberapa dekad yang lepas. Keperluan khusus untuk penyelidikan kakisan ini adalah untuk mengenal pasti keperluan elektrod rujukan pakai buang dan boleh dipercayai. Penyelidikan ini mengkaji keberkesanan elektrod rujukan berasaskan cecair dan keadaan pepejal yang merupakan prestasi pakai buang dan boleh dipercayai. Elektrod telah disediakan dengan menggunakan bahan kos rendah (pakai buang) dalam elektrod berasaskan cecair dan pepejal Sulfat Kuprum-Kuprum (CCS). Kestabilan potensi telah diuji untuk tujuan yang boleh dipercayai melalui kaedah pengukuran Potensi Litar Terbuka (OCP) pada spesimen konkrit rebar. Kelakuan rujukan keadaan pepejal dan elektrod rujukan berasaskan cecair dari segi polarisasi telah dikaji dalam persekitaran terhakis. Data potensi masa nyata juga diperoleh untuk kajian kadar kakisan. Hasilnya, kajian menunjukkan prestasi ketekalan nilai (OCP) semasa pengukuran kakisan. Sisi maksimum nilai potensi minimum kurang daripada 0.02 V menunjukkan bahawa elektrod kuprum (Cu) berasaskan cecair dan elektrod kuprum (Cu) keadaan pepejal boleh dipercayai, boleh disesuaikan dan boleh digunakan untuk pengukuran kakisan konkrit bertetulang. Hasil pengukuran polarisasi masa nyata menunjukkan bahawa kakisan berisiko tinggi berlaku pada rebar terbenam melalui proses pemvisualisasi secara langsung spesimen konkrit rebar. Oleh itu, kedua-dua elektrod rujukan pakai buang menunjukkan kestabilannya dan mengurangkan kos penyelidikan kakisan konkrit bertetulang.

Kata kunci: Analisis keupayaan; Cu/CuSO₄; elektrod rujukan; kakisan konkrit; sulfat kuprum-kuprum

INTRODUCTION

For centuries, concrete and cement solution materials have been among the main alternatives in various structure fields, whether civil structures, industry, or other public facilities. It is due to their durability, low porosity, and high-strength mechanical performance. Therefore, this material allowed infrastructure development, such as bridges, dams, industry, and offshore structures. The reinforcing steel embedded in the structures influences the strength and mechanical performance of concrete structures (Abdullah 2021; Huang et al. 2020). The proper design and composition of the embedded rebar influence the performance of its mechanical strength, as derived by Hortigon et al. (2018). The researchers mention that the concrete and cement solution serves as a shield for the rebar from the environment. Kainuma et al. (2018) have derived the differences in the corroded surface layer based on different environments. Nevertheless, such materials have natural electrochemical properties that degrade over time and are vulnerable to breaking. Among the fragilities are those related to corrosion on the reinforcing steel rebar (Bayuaji et al. 2018; Fonna et al. 2011; Ihsan et al. 2021). Aggressive penetration of the agent (chloride ions) can result in electrochemical contamination (Islami et al. 2017). The electrochemical penetration phenomenon also infiltrates the reinforcing steel. Moreover, the degradation of the insulating shell produced on the reinforcing steel significantly accelerated reinforcement corrosion, progressively affecting the performance of structures (Miah et al. 2020).

Many researchers pay more attention to reinforced concrete electrochemical analysis to overcome the problems (Senin et al. 2019). The electrochemical corrosion behaviour of the reinforced concrete has been reported by Park and Jung (2021). Corrosion occurs as a result of the addition of chloride ions to the cement and concrete solution (Khan, Ahmad & Al-Gahtani 2017). The instrument strength is affected by concrete behaviour, temperature (Wang, Camps-Arbestain & Hedley 2016), and liquid aggregate (Kurpinska & Haustein 2021).

Therefore, the monitoring of certain structures degradation is hence of significant importance, requiring proficient performance measurements without disturbing concrete structures. In field identification, an issue occurs when a reference electrode is used to evaluate the potential of corroded rebar. The potential of the reinforced concrete measured is related to an electrode distribution determined by its structure, a cell in which one electrode is the reinforced rebar and the other is a reference electrode. Such a situation presents several challenges. As a result, many researchers (Hall

et al. 2016; Sophocleous & Atkinson 2017; Stern, Sadoway & Tester 2011; Subbiah et al. 2017) have established concepts using various reference electrodes. The Standard Hydrogen Electrode (SHE) has been preferred as a standard reference electrode analysis process. SHE references are used for determining potential in electroplating, batteries, catalytic hydrogenation, and hydrometallurgy (Szabo & Bakos 2010). A leakage problem was identified, resulting in pollution and influencing the potential collected value on rebars embedded in concrete. The Ag/AgCl reference electrode is also one of the most common reference electrodes used in corrosion investigation research. In addition, the reference electrode is capable of measuring the potential distribution within the corrosion specimen (Alva et al. 2018; Sophocleous & Atkinson 2017). Although the high fabrication cost of Ag/AgCl electrodes is a limitation of these materials.

The Cu/CuSO₄ electrode is a widely used solution reference electrode for reliable and disposable electrodes for reinforced concrete potential analysis (Ihsan et al. 2021b; Ross 1992). The Cu/CuSO₄ electrode is commonly used in field corrosion protection of buried metals, such as building foundations and storage tanks. As a result, the primary research focuses on on-field performance rather than laboratory measurement, where precise electrochemical data is required. The potential data collection in reinforced concrete corrosion is influenced by the concrete cover environment. The Copper-copper Sulphate (CCS) electrode is one of the reference electrode solutions for investigating steel reinforcement potential corrosion based on electrical conductivity, thermal conductivity, corrosion resistance, and electrolyte contamination. Therefore, this paper focuses on the CCS reference electrode for potential detection on carbon steel.

As a result, the performance of CCS *liquid-based* reference electrodes and *solid-state* reference electrodes has been investigated. The reference electrode was designed and resized for disposable reference electrodes using a low-cost assembly process. The consistency and performance of the Open Circuit Potential (OCP) value during potential measurement were investigated. The real-time potential data was also obtained for the corrosion rate investigation. Both reference electrodes were able to determine the anode and cathode potential values for the reinforced concrete corrosion investigation. The result also shows the stability of both the reference electrode and the OCP value during the measurement. The CCS *liquid-based* and *solid-state* reference electrodes perform well for the potential distribution value of reinforced concrete. It can be inferred that the CCS *liquid-*

based and solid-state reference electrodes are highly recommended for reliable and disposable reinforced concrete field experiments.

MATERIALS AND METHODS

The copper material has been extensively used in various applications around the world for its industrial and structural properties. They have good strength and outstanding corrosion resistance due to their excellent electrical and thermal conductivities. Of all the common metals, copper material possesses one of the highest electrical and thermal conductivities (Hamid et al. 2022; Ross 1992). In a sense, copper material was a promising material due to its low cost, abundance, and excellent conductivity for electrochemical corrosion detection (Kadiman et al. 2018).

Copper (Cu) and silver (Ag) had the highest electrical conductivity transfer in Table 1. However, the high cost of silver (Ag) and rare materials makes their use impractical in routine practise or industry. Consequently, reliable, accurate, and abundant materials were required for potential measurement in the field. Therefore, copper is still a prominent material for industrial property investigation and research. Copper was identified as the potential consisting detector in corrosion potential investigation research, along with a copper-copper sulphate (CCS) electrode solution.

Much of the CCS literature derives from research investigating the activity coefficients of aqueous species or circumstances associated with field applications (Ceocor Working Group Publication 2018; Stern,

Sadoway & Tester 2011). Referring to the Ag/AgCl reference electrode, the copper reference electrode consists of an aqueous (aq) solution and a copper solid(s) wire to form the electrochemical couple. The dissolved solution is commonly CuSO₄(aq) mixed with H₂SO₄(aq), and the Cu(s) wire is a common and well-known liquid-based reference electrode. Considering many researchers previous results, CCS has a high material potential value collecting ability. However, it should be noted that the liquid CCS gradually loses some CuSO₄ content after collection due to porosity. Owing to this drawback, Cu²⁺ ion activity is no longer constant, but first it increases, and then after reaching the peak range, it slowly decreases. Therefore, the equilibrium potential of the liquid CCS was investigated by Stern, Sadoway and Tester (2011).

Besides, regarding pressure resistance and temperature range, the liquid CCS application field is also severely limited. In the high-temperature analysis, the CCS solution heats or reacts with the reference system; once at a low temperature, the electrolyte freezes and influences its determining performance. It states that up to 0.1 mol/kg CCS concentrations are possible, and the reference electrode remains constant at a certain temperature. It can be inferred that the CCS reference electrode is expectant in a particular field. The Cu ion concentration in the sulphate solution is not lower than 0.1 mol/kg and is higher in certain temperature ranges. Therefore, the liquid-based CCS is considered a promising solution for reliable potential determination, considering its remaining lifetime and field temperature.

TABLE 1. Material electrical conductivity

Electrode material	Electrical conductivity (at 20 °C)	References
Copper (Cu)	5.96×10^7	Kachhap, Singh & Debnath 2018; Kim et al. 2018
Gold (Au)	4.10×10^7	Heard & Lennox 2020
Silver (Ag)	6.30×10^7	Baudler et al. 2015
Titanium (Ti)	2.38×10^7	Manu et al. 2021; Xu et al. 2016
Tungsten (W)	1.79×10^7	Das et al. 2012; Yakovleva et al. 2018
Indium-tin-oxide	1.3×10^7	Al-Kuhaili 2020
Graphene	1.0×10^7	Karami et al. 2021

TABLE 2. Potential of CCS electrode regarding the concentration (Szabo & Bakos 2010)

Copper sulphate concentration (mol/kg)	Copper-copper sulphate potential electrode (Volt)
Saturated	0.317
1.0	0.337
0.1	0.307
0.01	0.277

Furthermore, many researchers also developed the solid-state CCS reference electrode. The developed *solid-state* CCS is required to solve the liquid-based CCS electrode remaining lifetime problem. The ideal solid CCS must have identical characteristics and good performance, such as a *liquid-based* CCS electrode. The *solid-state* CCS electrode must also have long-term durability and stability. Guth et al. (2009) inferred that the main problem to be considered in order to realize such a *solid-state* reference electrode is the connection of an ion-conducting (aqueous) solution with an electronic conductor. As a result, some *solid-state* reference

electrodes, such as the *solid-state* Cu/CuSO₄ reference electrode, are currently available with their properties.

According to Table 3, copper solid-state reference electrodes consisting solely of solid copper substance (Cu Crystal) rather than any liquids or solidified solutions are the most promising solution for reference electrode systems. As a matter of fact, the existence of liquid solution components such as the inner electrolytic permits measurements in extended temperature and pressure ranges as well as in non-aqueous solutions with disposable and low-cost reference materials.

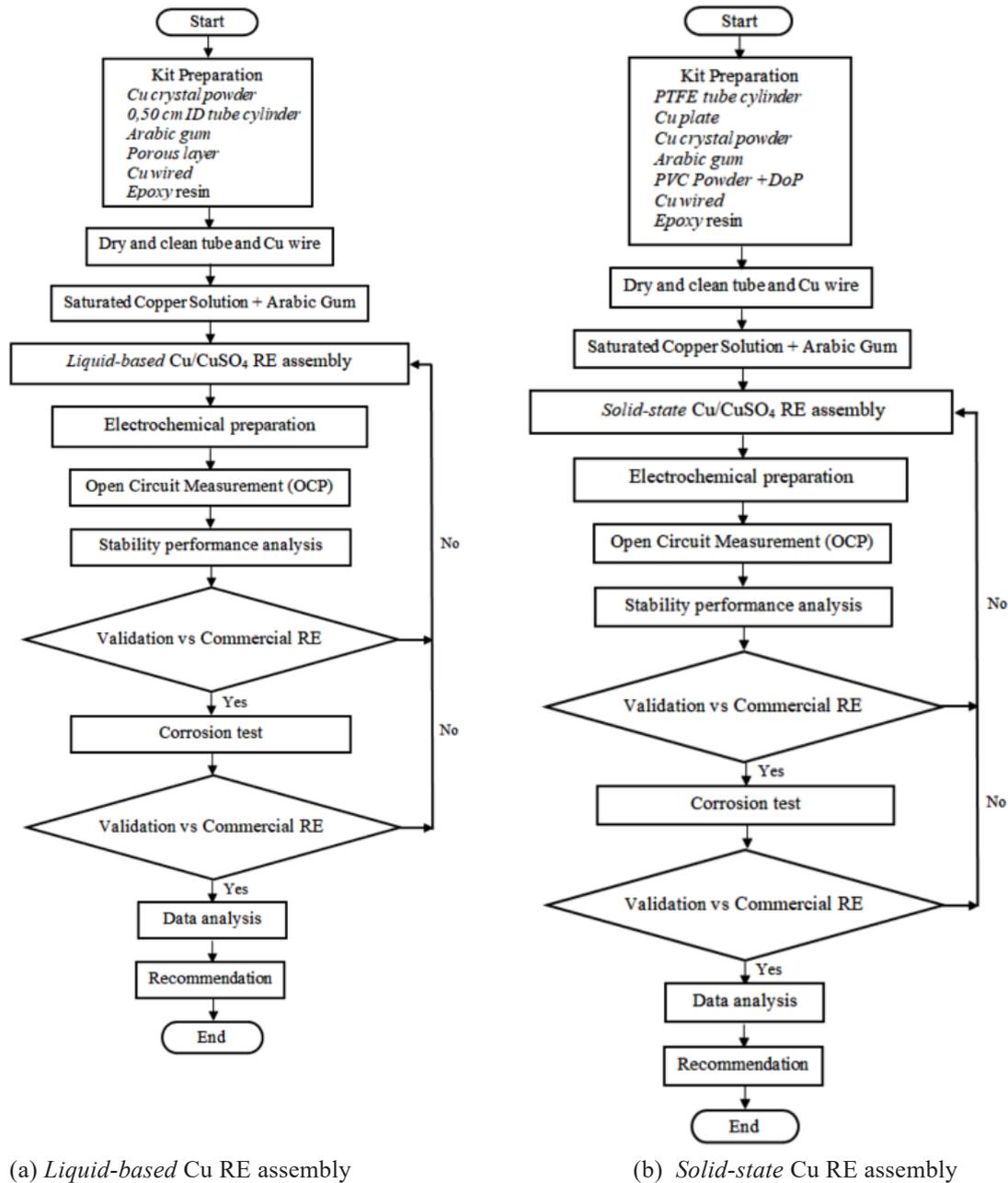


FIGURE 1. Flow chart *Liquid-based* and *Solid-state* Reference Electrode assembly

In this paper, *liquid-based* and *solid-state* reference electrodes have been miniaturized or size reduced. Changing the phase of the existing electrolyte solution is required. Take note that the miniaturized process is based on initial studies (Baudler et al. 2015; Hall et al. 2016; Maryoto et al. 2018; Xu et al. 2016). The liquid phase and solid phase have been calibrated by several Ag/AgCl commercial reference electrodes. This *liquid-based* and *solid-state* electrode has several effectiveness, including an efficient fabrication process, reliability, disposable nature, and the ability to be mass-produced.

Moreover, the size of the electrodes can be modified as needed for embedding into reinforced concrete. Therefore, this work must develop many reference electrodes for stability analysis. Also, an initial study was conducted on the development of a simple reference electrode in terms of potential corrosion analysis on reinforced concrete. The flowchart of the *liquid-based* and *solid-state* Cu RE is shown in Figure 1. Table 4 also shows the costs of raw materials for the reference electrode assembly.

TABLE 3. Copper (Cu) electro & mechanical properties (Maina et al. 2018)

Melting temperature	1356 K
Thermal conductivity	391.1 W (m K)
Density	8.94 g/cm ³
Electrical resistivity	17.1 nΩ.m
Electrical conductivity	59.1 MS/m
Poisson's ratio	0.33
Young's modulus	120 GPa

TABLE 4. *Liquid-based* and *solid-state* Reference electrode assembly cost

(a) *Liquid-based* Reference Electrode assembly cost

No	Material		Price
1	Cu-crystal powder	50 mg	\$ 2
2	0.50 cm ID tube cylinder	10 pcs	\$ 3
3	Porous layer	1 pack	\$ 1
4	Arabic gum	1 pack	\$ 5
5	Epoxy resin	1 pack	\$ 2
Total assembly cost liquid-based RE			\$ 13

(b) *Solid-state* Reference electrode assembly cost

No	Material		Price
1	Cu-crystal powder	50 mg	\$ 2
2	PTFE tube cylinder	1 m	\$ 5
3	Copper Plate	10 × 10 × 0.2 cm	\$ 10
4	PVC Powder + DoP	50 mg	\$ 14
5	Arabic gum	1 pack	\$ 5
6	Epoxy resin	1 pack	\$ 2
Total assembly cost			\$ 38

LIQUID-BASED Cu REFERENCE ELECTRODE (RE)

The design of resized *liquid-based* Cu reference electrode, as shown in Figure 2(a) is provided by employing a plastic cylinder 0.50 cm in diameter by 3 cm in length. Based on Szabo's literature, the copper sulphate solution is saturated sulphate and also contains crystalline copper in the plastic tube. Subsequently, to prevent leakage problems from previous research, the combination of saturated sulphate solution with *arabic gum* can change the liquid phase into a solid-liquid jelly. With this method, leakage can be solved without affecting the *Liquid-based* Cu RE performance for conductivity detection, as shown in Figure 2(b).

Furthermore, a dense porous cotton cover was plugged in at one end of the tube with a diameter of 0.2 cm. Therefore, the contact between the copper sulphate electrolyte and the specimen electrolyte can be connected. Furthermore, on the other hand, the copper wire without a sheath on the inside of the tube is coated with an epoxy adhesive cover so that there is no

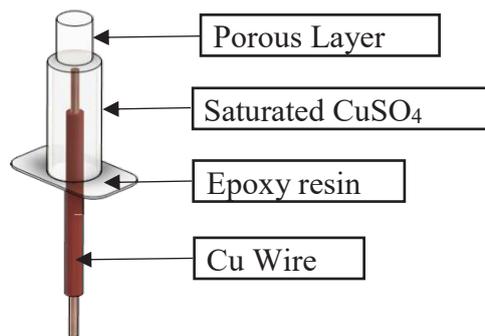
leakage and it is not contaminated with other electrolytes. Furthermore, the outer copper wire of the sulphate tube is left shrouded until the end of the wire is attached to the reference voltmeter.

In this research, 10 *Liquid-based* Copper electrode was obtained for Open Circuit Potential (OCP) measurement on the ferrous material, as shown in Figure 3. The OCP value was detected to analyze the stability and reliability of the miniatures liquid Cu reference electrode. The resizing liquid reference electrode electrolyte OCP value was analyzed during 600 cycling times without current.

SOLID-STATE Cu REFERENCE ELECTRODE (RE)

The solid-state Cu reference electrode was a cleaned copper plate measuring 10×10 mm and 2 mm thick. The Cu plate was polished and cleaned with distilled water and dried.

The $6 \times$ OD 8 mm PTFE tube ID was paired with epoxy resin gum on the Cu plate and dried at room temperature. During the process of dehydrating



(a) Desain liquid-based Cu Reference Eelctrode



(b) Liquid-based Cu Reference Electorde

FIGURE 2. Desain and miniaturized dimension of Liquid-based Cu Reference Electrode

FIGURE 3. 10 sample liquid-based Cu/CuSO₄ reference electrode

the PTFE tube and copper plate form, ions are diffused out by containing 5 mg of crystal-saturated copper sulphate. A cube cover made of 35 mg + 65 mg Poly Vinyl Chloride (PVC) and Dioctadecyloxycarbocyanine (Dioc) submerged in Tetrahydrofuran (THF) protects copper sulphate crystals (Figure 4).

Later on, the liquid resized RE was exposed after drying overnight at room temperature. Subsequently, Cu wire was applied to access the selected solid RE in order to distribute the potential value to the potential machines test. The reference surface was mounted with epoxy resin, excluding the PVC + Dioc membrane. After the solid-state RE was performed, the reinforced concrete potential was measured by the Open Circuit Potential (OCP) method (Figure 5).

RESULTS AND DISCUSSION

OPEN CIRCUIT POTENTIAL MEASUREMENT

Under the normal ferrous condition, the potential distribution value was analyzed using *liquid-based Cu*

RE, *solid-state Cu* RE, and validated with Ag/AgCl reference electrodes. The cleaned ferrous with 10×10 mm dimensions was prepared (Dewi et al. 2021). In the analysis, portable ZIVE PPI potential metre was attached to an electrochemical cell to measure the potential value. The potential data was measured with zero current. This first experiment aims to analyze the stability of the resizing reference electrode for potential value collecting data. The potential measurement cycle was collected for 600 cycles and repeated for the following reference electrode. The potential measurement cycle time was determined based on the stability equipment testing environment by the potential meter. Subsequent, the testing procedure was repeated for the other reference electrode for rebar potential measurement.

All the miniatures reference electrode were shown in Figure 6. The standard procedure of potential measurement using open circuit potential measurement was applied during the experiment. The stability performance regarding the potential collecting data after 600 cycle time. The *liquid-based* reference electrode in

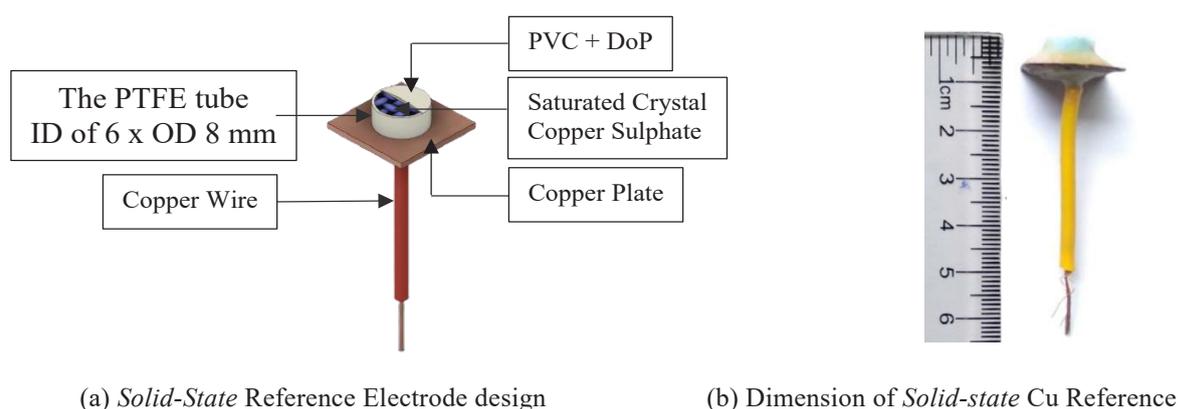


FIGURE 4. Design and dimension of Liquid-based Cu Reference Electrode

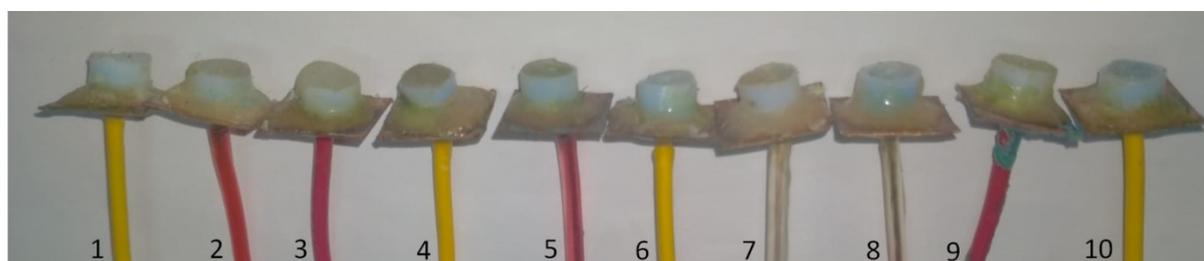


FIGURE 5. *Solid-state* Cu reference electrode

Figure 6(a) shows the linear potential value after 600 measurement cycling-time by 10 miniatures specimen without current distribution. The collected potential deviation value in the range -0.1 V for all samples. The *solid-state* Cu reference electrodes also show similar behaviour potential collected value in Figure 6(b). Collected data were resulted from only -0.1 Volt differences regarding OCP measurements.

The detail value of stability liquid-based and solid-state Cu reference was reported by the Open Circuit Potential (OCP) measurement as shown in Figure 7. The stability range of the OCP solid-state Cu RE range value from maximum to minimum less than 0.0043 V and the deviation of all potential data is 0.001 V as shown in Figure 7(a). Furthermore, the resemblance behaviour was shown by the 600 cyclings OCP result by the liquid-based RE in Figure 7(b). The potential data range resulting from the liquid-based Cu RE is more diminutive than 0.0046 V. The minimum potential value was -0.7535 V, and the maximum was -0.7578 V.

Meanwhile, the deviation of potential value is only 0.0013 V. It indicates that the references show promising stability performance based on the resulting data.

In addition, a validation investigation employing a commercial Ag/AgCl reference electrode was presented in Figure 8. During the OCP test, the Ag/AgCl reference electrode (commercial) showed a comparable linear maximum potential of -0.7881 V. Meanwhile, the minimum potential OCP value at -0.7720 V. The potential value range was 0.0162 V. Furthermore, the deviation of all potential data was 0.004 V. Regarding previous research by Islami (2016), the flux range of the potential value during Open Circuit Potential measurement must be less than 0.02 V which is the maximum to the minimum potential value.

According to Table 5, all references indicate that the model demonstrates stability during measurement. All potential differences among references were less than 0.1 volts. It indicates that the resizing of the Cu reference electrode proves its stability and effectiveness in measuring the potential on the concrete rebar.

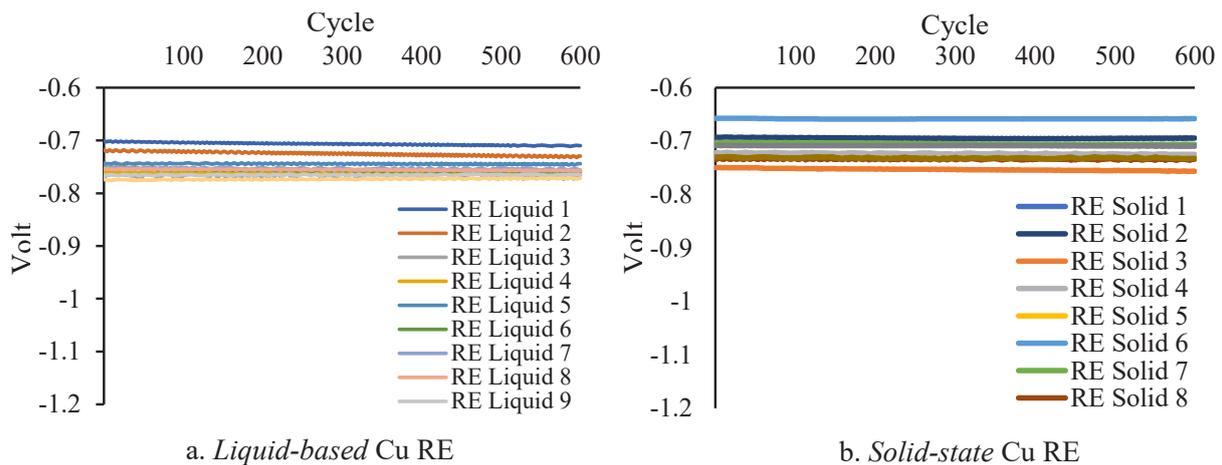


FIGURE 6. OCP value by 10 sample of (a) *Liquid-based* Cu and (b) *Solid-state* Cu RE

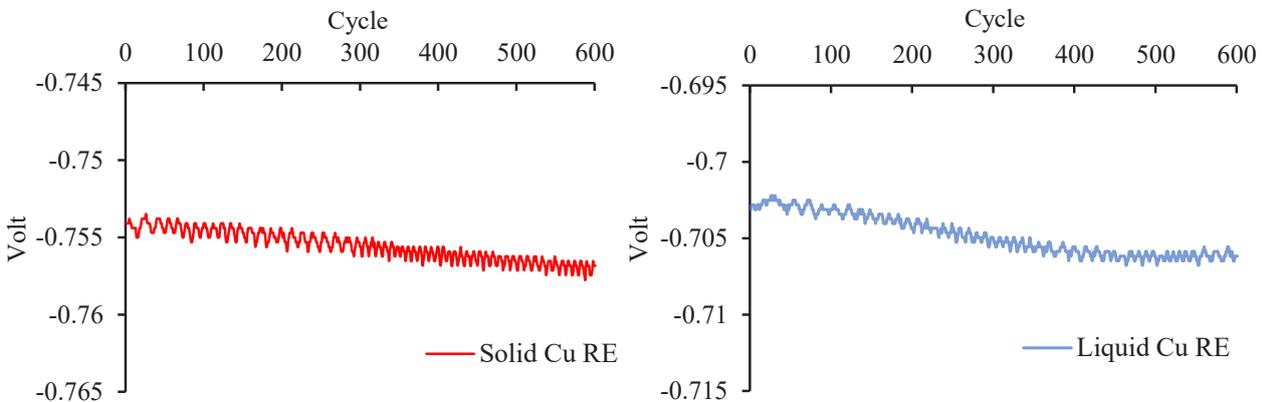


FIGURE 7. The Stability of OCP test by (a) *Solid-state* Cu RE, (b) *Liquid-based* Cu RE

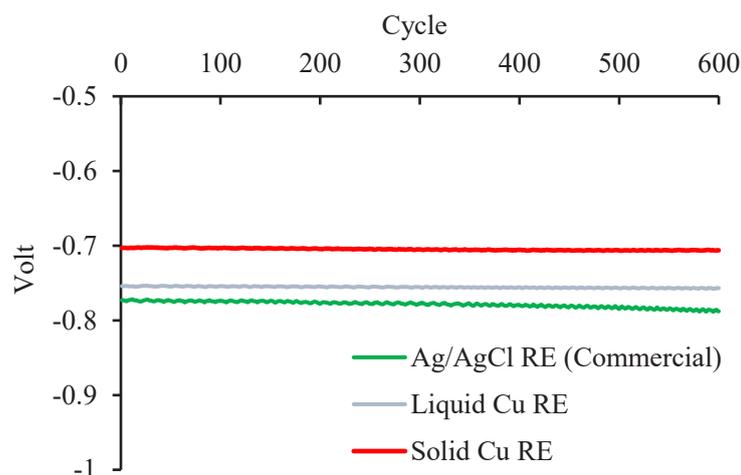


FIGURE 8. Validation Stability of OCP test by Solid-state Cu RE, Liquid-based Cu RE vs Ag/AgCl Commercial Reference Electrode

TABLE 5. Potential Range & Deviation value of the OCP measurement (Saturated Hydrogen Electrode Standard)

Potential	Liquid RE	Solid RE	AgCl RE
Value	V	∓ V	V
Min	-0.7535	-0.7022	-0.7720
Max	-0.7578	-0.7068	-0.7881
Range	0.0043	0.0046	0.0162
Deviation	0.0010	0.0013	0.0040

POLARIZATION BEHAVIOUR (E_{corr} and I_{corr})

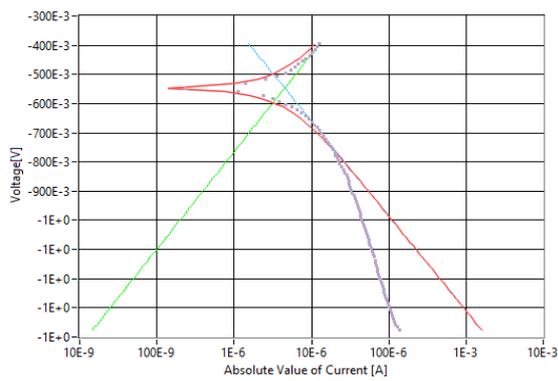
The polarisation behaviour performed the rebar corrosion rate analysis for the liquid Cu reference and the solid Cu reference. The specimen of corroded reinforced rebar was prepared for corrosion rate analysis. For instance, the potential difference between the cathode and the anode was determined by the reference electrodes. The corrosion rate that occurs is expressed based on the correlation of the voltage curve (E_{corr}) and current function (I_{corr}), known as the polarisation curve, which provides insight into the phenomenon. The corrosion rate inside the polarisation curve is quantified by considering the values of E_{corr} and I_{corr} . The determination of E_{corr} and I_{corr} from the polarisation curve can be estimated by the Tafel Equation.

The Tafel experimental reference electrode's polarisation behaviour results from the Tafel value as shown in Table 6. The *liquid-based* Cu RE, *solid-state* Cu RE, and commercial Ag/AgCl reference electrodes all demonstrated similar behavior in terms of corrosion potential (E_{corr}) and corrosion current (I_{corr}). E_{corr} and I_{corr} data was analyzed by using Tafel analyses from IVMAN software as shown in Figure 9.

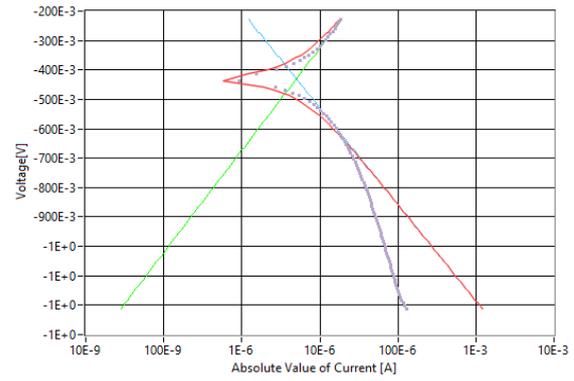
The solid-state Cu reference electrode measures a less negative potential than the liquid-based Cu and commercial Ag/AgCl reference electrode. The analysis showed a similar level of corrosion risk in accordance with ASTM 876 corrosion risk criteria as shown in Table 7.

TABLE 6. Tafel corrosion analysis by using the reference electrode

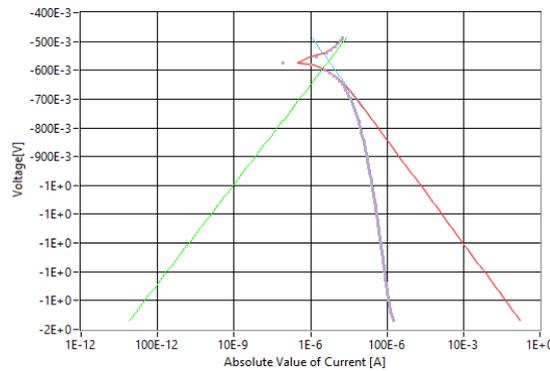
Reference Electrode	E _{corr} mV	I _{corr} μA
Liquid-based RE	-546,803	6,093
Solid-state RE	-556,198	4,505
Ag/AgCl (commercial)	-426,497	2,844



(a) mV Vs μA liquid-based RE



(b) mV Vs μA Ag/AgCl (commercial)



(c) mV Vs μA Solid-state RE

FIGURE 9. E_{corr} and I_{corr} Reference Electrode analysis

TABLE 7. ASTM C876-91, 1999

Rebar potential (mV)		Qualitative risk of corrosion
Cu/CuSO ₄ electrode	Ag/AgCl electrode	Likely corrosion condition
> - 200	> - 106	Low (10% risk of condition)
- 200 to -350	- 106 to -256	Intermediate corrosion risk (uncertain)
< - 350	< - 256	High (> 90% risk of corrosion)
< - 500	< - 406	Severe corrosion

The corrosion potential (E_{corr}) of the solid-state Cu/CuSo₄ reference electrode is -556,198 mV, and the corrosion current density (I_{corr}) is 2,844 A. In contrast, the liquid-based Cu reference electrode exhibited a distinct potential value. the corrosion potentials (E_{corr}) were -546,803 mV and the current density (I_{corr}) was 4,505 μ A, respectively. The Ag/AgCl commercial reference electrode also denotes the corrosion potential (E_{corr}) at -426,497 mV and the corrosion current density (I_{corr}) at 6,093 μ A. All Tafel analyses indicate that the rebar was corroded severely.

Figure 10 shows the Tafel potential anode and cathode area for corrosion propagation. The result can describe similar behaviour of the anode and cathode areas by using the *liquid-based* reference electrode, *solid-state* reference electrode and Ag/AgCl references. The Similar behaviour of Tafel analysis has been shown by Figure 10. The Cu reference shows close behaviour, whereas the Ag/AgCl reference shows a different potential value. Still, the reference shows a similar trend in Tafel's analysis. Duffo and

Farina (2009) noted that the potential value depends on the environment, electrolyte, and stability of the OCP resulting by reference. It is indicated that the environment and electrolyte influence the potential value.

Furthermore, Figure 11 captures the visual representation of the corroded rebar after the mechanical process for visualizing the corroded reinforcement bars. The resizing and compact size of the copper reference electrode can be inferred to be applicable for the reinforced concrete corrosion analysis. The developed reference electrode can be incorporated into an embedded reference electrode model for real-time potential data collection on reinforcing steel. Both the developed reference electrode and the commercial electrode demonstrated comparable corrosion investigation results. Nevertheless, the developed reference electrode model's research cost differs significantly from the commercial reference electrode. The resized reference electrode could be used for a reliable, low-cost, and disposable analysis of corrosion in reinforced concrete.



FIGURE 10. Validation potential Tafel plot by liquid-based Cu RE, solid-state Cu RE vs Ag/AgCl (commercial) Reference Electrode

CONCLUSION

The enlarged reference electrode was designed to collect a disposable, dependable, and cost-effective efficacy reference electrode. Regarding the performance evaluation of reference electrodes, a low-cost assembly procedure was introduced. *Copper-copper sulphate* (CCS) was utilised for *liquid-based* and *solid-state* re-assembly reference electrodes for corrosion reinforced concrete. The Open Circuit Potential (OCP) stability

performance of both design references was analysed. The findings indicate the consistency, dependability, and linearity of the OCP measurement for 10 reference electrode samples. 600 cycle time measurements have proven the reliability of the resized reference. The result of both reference deviations of potential value was less than 0,02 V. Both references have been validated with an Ag/AgCl commercial reference electrode and showed similar behaviour as a result of the experiment.

The reference displays the performance employing Tafel measurement for real-time potential analysis. The result represents the real-time potential anode-cathode area in terms of corrosion behaviour. Furthermore, similar behaviour was seen for all analyses utilizing the commercial and well-established Ag/AgCl reference electrode. The miniaturized reference electrode was shown to be valid due to the findings. As a result, the disposable reference electrode can be manufactured using *liquid-based* or *solid-state* Cu/CuSO₄, which reduces the cost of research for corrosion analysis of reinforced concrete rebar. For measuring reinforcing steel potential, *liquid-based* and *solid-state* Cu/CuSO₄ reference electrodes can overcome commercial reference electrode restrictions.

ACKNOWLEDGEMENTS

This work was supported by Ministry of Education, Culture, Research, and Technology, Republic of Indonesia, Penelitian Dasar (PD) No. 552/UN11.2.1/PT.01.03/DRPM/2023.

REFERENCES

- Abdullah, J.A. 2021. Finite element modelling of CFRP wrapped concrete specimens subjected to localised axial compression. *Jurnal Kejuruteraan* 33(4): 1123-1137.
- Alva, S., Binti Abdul Aziz, A.S., Bin Syono, M.I. & Bin Wan Jamil, W.A. 2018. Ag/AgCl reference electrode based on thin film of arabic gum membrane. *Indonesian Journal of Chemistry* 18(3) 479-485.
- Al-Kuhaili, M.F. 2020. Electrical conductivity enhancement of indium tin oxide (ITO) thin films reactively sputtered in a hydrogen plasma. *Journal of Materials Science: Materials in Electronics* 31(4): 2729-2740.
- Baudler, A., Schmidt, I., Langner, M., Greiner, A. & Schröder, U. 2015. Does it have to be carbon? Metal anodes in microbial fuel cells and related bioelectrochemical systems. *Energy Environment Science* 8(7): 2048-2055.
- Bayuaji, R., Darmawan, M.S., Husin, N.A., Anugraha, R.B. & Budipriyanto, A. 2018. Corrosion damage assessment of a reinforced concrete canal structure of power plant after 20 years of exposure in a marine environment: A case study. *Engineering Failure Analysis* 84: 287-299.
- Ceacor Working Group Publication. 2018. Reference electrodes for monitoring cathodic protection on buried pipelines pre-standard. *Ceacor Working Group Publication*. pp. 1-32.
- Das, P.R., Pati, B., Sutar, B.C. & Choudhury, R.N. P. 2012. Study of structural and electrical properties of a new type of complex tungsten bronze electroceramics. *Journal of Modern Physics* 3(8): 870-880.
- Dewi, M.S., Alva, S. & Wan Jamil, W.A. 2021. Development and characterization of solid Cu/CuSO₄ reference electrodes. *International Journal of Innovation in Mechanical Engineering and Advanced Materials* 3(1): 17-25.
- Duffo, G.S. & Farina, S.B. 2009. Development of an embeddable sensor to monitor the corrosion process of new and existing reinforced concrete structures. *Construction and Building Materials* 23(8): 2746-2751.
- Fonna, S., Ridha, M., Huzni, S., Israr, & Ariffin, A.K. 2011. Boundary element inverse analysis by using particle swarm optimization for reinforced concrete corrosion identification. *Advanced Materials Research* 339: 171-175.
- Guth, U., Gerlach, F., Decker, M., Oelbner, W. & Vonau, W. 2009. Solid-state reference electrodes for potentiometric sensors. *Journal of Solid State Electrochemical* 13(1): 27-39.
- Hall, D.M., Beck, J.R., Brand, E., Ziomek-Moroz, M. & Lvov, S.N. 2016. Copper-Copper sulfate reference electrode for operating in high temperature and high pressure aqueous environments. *Electrochimical Acta* 221: 96-106.
- Hamid, K., Badarisman, A., Jalar, A. & Abu Bakar, M. 2022. Investigation of integrated factors in the occurrence of copper wire bonding corrosion of semiconductor packages. *Journal of Physics: Conference Series* 2169: 012016.
- Heard, D.M. & Lennox, A.J.J. 2020. Electrode materials in modern organic electrochemistry. *Angewandte Chemie International Edition* 59(43): 18866-18884.
- Hortigón, B., Ancio, F., Nieto-García, E.J., Herrera, M.A. & Gallardo, J.M. 2018. Influence of rebar design on mechanical behaviour of tempcore steel. *Procedia Structural Integrity* 13: 601-606.
- Huang Jiandong, Rayed Alyousef, Suhatriil Meldi, Shahrizan Baharom, Hisham Alabduljabbar, Abdulaziz Alaskar & Hamid Assilzadeh. 2020. Influence of porosity and cement grade on concrete mechanical properties. *Advances in Concrete Construction* 10: 393-402.
- Ihsan, M., Fonna, S., Islami, N., Faizar, & Ariffin, A.K. 2021a. Simulation of corrosion field measurement on reinforced concrete using BEM. *Journal of Mechanical Engineering and Science* 15(2): 8072-8081.
- Ihsan, M., Fonna, S., Huzni, S., Islami, N. & Ariffin, A.K. 2021b. Cu/CuSO₄ solid-state reference electrode for potential corrosion measurement on the reinforcin steel. *Proceedings of the 3rd International Conference on Experimental and Computational Mechanics in Engineering*. pp. 328-339.
- Islami, N. 2016. Corrosion polarization mechanism in 3,5% sodium chloride under mechanical loading. Bangi: Universiti Kebangsaan Malaysia (Unpublished).
- Islami, N., Rashid, S., Ariffin, A.K. & Nuawi, M.Z. 2017. Stress corrosion damage on austenitic stainless steel in sodium chloride. *International Journal of Automotive and Mechanical Engineering* 14(1): 3824-3836.
- Kachhap, S., Singh, A. & Debnath, K. 2018. Electric discharge drilling of hybrid metal matrix composites using different tool electrodes. *Journal of Scientific & Industrial Research* 77(6): 325-329.
- Kadiman, N.N., Rashid, M.O.A., Muhamad, N. & Sulong, A.B. 2018. Effects of sintering temperature on the physical and mechanical properties of injection-molded Copper/Graphene composite. *Journal of Advanced Manufacturing Technology* 12(1): 49-60.

- Kainuma, S., Yamamoto, Y., Ahn, J.H. & Jeong, Y.S. 2018. Evaluation method for time-dependent corrosion depth of uncoated weathering steel using thickness of corrosion product layer. *Structural Engineering Mechanics* 65(2): 191-201.
- Karami, Z., Youssefi, M., Raeissi, K. & Zhiani, M. 2021. Effect of the morphology of silver layer on electrical conductivity and electrochemical performance of silver/reduced graphene oxide/cotton fabric composite as a flexible supercapacitor electrode. *Journal of Energy Storage* 42: 103042.
- Khan, M.U., Ahmad, S. & Al-Gahtani, H.A. 2017. Chloride-induced corrosion of steel in concrete: An overview on chloride diffusion and prediction of corrosion initiation time. *International Journal of Corrosion* 2017: 5819202.
- Kim, G.H., Kim, K., Lee, E., An, T., Choi, W., Lim, G. & Shin, J.H. 2018. Recent progress on microelectrodes in neural interfaces. *Materials (Basel)* 11(10): 1995.
- Kurpińska, M. & Haustein, E. 2021. Experimental study of the resistance to influence of aggressive liquids on lightweight concrete. *Materials (Basel)* 14(15): 4185.
- Maina, M.R., Okamoto, Y., Inoue, R., Nakashiba, S., Okada, A. & Sakagawa, T. 2018. Influence of surface state in micro-welding of copper by Nd:YAG laser. *Applied Science* 8(12): 2364.
- Manu, K., Jezierski, J., Sai Ganesh, M.R., Shankar, V. & Narayanan, S.A. 2021. Titanium in cast Cu-Sn alloys - A review. *Materials (Basel)* 14(16): 4587.
- Maryoto, A., Gan, B.S., Hermanto, N.I.S. & Setijadi, R. 2018. The compressive strength and resistivity toward corrosion attacks by chloride ion of concrete containing Type I cement and calcium stearate. *International Journal of Corrosion* 2018: 2042510.
- Miah, M.J., Hossain Patoary, M.M., Paul, S.C., Babafemi, A.J. & Panda, B. 2020. Enhancement of mechanical properties and porosity of concrete using steel slag coarse aggregate. *Materials (Basel)* 13(12): 2865.
- Park, J. & Jung, M. 2021. Evaluation of the corrosion behavior of reinforced concrete with an inhibitor by electrochemical impedance spectroscopy. *Materials (Basel)* 14(19): 5508.
- Ross, R.B. 1992. Copper Cu. In *Metallic Material Specification Handbook*. Boston: Springer. pp. 94-170.
- Senin, S.F., Hamid, R., Ahmad, J., Rosli, M.I.F., Yusuff, A., Rohim, R., Abdul Ghani, K.D. & Mohamed Noor, S. 2019. Damage detection of artificial corroded rebars and quantification using non-destructive methods on reinforced concrete structure. *Journal Physics Conference Series* 1349(1): 012044.
- Sophocleous, M. & Atkinson, J.K. 2017. A review of screen-printed silver/silver chloride (Ag/AgCl) reference electrodes potentially suitable for environmental potentiometric sensors. *Sensors Actuators: A Physical* 267: 106-120.
- Stern, H.A.G., Sadoway, D.R. & Tester, J.W. 2011. Copper sulfate reference electrode. *Journal of Electroanalytical Chemistry* 659(2): 143-150.
- Subbiah, K., Lee, H.S., Lee, Y.S., Kumar Singh, J., Kwon, S.J. & Natarajan, R. 2017. Fabrication of a cerium-doped nickel ferrite solid-state reference electrode and its performance evaluation in concrete environment. *Sensors Actuators B: Chemical* 251: 509-523.
- Szabó, S. & Bakos, I. 2010. Reference electrodes in metal corrosion. *International Journal of Corrosion* 2010: 756950.
- Xu, B., Sohn, H.Y., Mohassab, Y. & Lan, Y. 2016. Structures, preparation and applications of titanium suboxides. *RSC Advanced* 6(83): 79706-79722.
- Yakovleva, G.E., Romanenko, A.I., Berdinsky, A.S., Kuznetsov, V.A., Ledneva, A.Y. & Fedorov, V.E. 2018. The research of temperature dependences of electrical conductivity and thermopower of WS₂ and WSe₂ with partial replacement of W on Nb. *Journal of Siberian Federal University – Mathematics and Physics* 11(4): 459-464.
- Wang, T., Camps-Arbestain, M. & Hedley, H. 2016. Factors influencing the molecular composition of soil organic matter in New Zealand grasslands. *Agricultures, Ecosystem & Environment* 232: 290-301.

*Corresponding author; email: syarizal.fonna@unsyiah.ac.id