A Novel Accelerated Corrosion Test for Supporting Devices in a Floating Photovoltaic System

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Abstract: Recently, countries from around the globe have been actively developing a new solar power system, namely, the floating photovoltaic (FPV) system. FPV is advantageous in terms of efficiency and cost effectiveness; however, environmental conditions on the surface of water are harsher than on the ground, and the regulations and standards for the long-term durability of supporting devices are insufficient. As a result, this study aims to investigate the durability of supporting devices through a novel type of accelerated corrosion test, copper-accelerated acetic acid salt spray (CASS). After an eight-day CASS test, the results demonstrated that only a small area of white protective layer on the SUPERDYMA shape steel was fully corroded and rusted. Moreover, five types of screw, fastened solidly on the SUPERDYMA shape steel, namely a galvanized steel screw capped with a type 316 stainless steel (SS) nut, a type 304 SS screw, a type 410 SS screw, a chromate-passivated galvanized steel screw, and a XP zinc–tin alloy coated steel screw, achieved varying degrees of rust. In general, the corrosion degree of the eight-day CASS test was more serious than that of the 136-day neutral salt spray (NSS) test. Therefore, the CASS test is faster and more efficient for the evaluation of the durability of supporting devices.

Keywords: floating photovoltaic (FPV); supporting device; durability; copper-accelerated acetic acid salt spray (CASS)

1. Introduction

Over recent years, the market of photovoltaic systems has been expanding rapidly. In addition to common types of rooftop, ground-mounted, and building-integrated photovoltaic systems, countries from around the world have been actively developing a floating photovoltaic (FPV) system, which is mainly installed on surface of idle waters [1,2]. The FPV system is highly suitable for countries that are densely populated and are highly dependent on imported energy, and it is expected to solve the development dilemma of insufficient land resources [3,4]. Single-pile fixed systems or dual-pile fixed systems are suitable for shallow water or small water level changes, while floating systems with support or floating systems without support are suitable for deep water or large water level changes, as depicted in Figure 1. The common materials of supporting devices are hot-dipped galvanized steel or aluminum. Concrete piles are generally used in fixed systems and are piled into the ground directly under water. The materials used in floating systems are mainly engineering plastics, most of which are high density polyethylene (HDPE) [5].
Taiwan is surrounded by seas. A high temperature and humid environment coupled with air pollutants make metal supports, retainers, and screws corrode easily in the atmosphere, as shown in Figure 2a. Because of strong northeast monsoons, some solar panels are loosened and even fall off, as shown in Figure 2b. The corrosivity of the atmosphere is graded by six levels in ascending order, including C1 (very low), C2 (low), C3 (medium), C4 (high), C5 (very high), and CX (extreme) [6]. Based on the grading diagram for the corrosion rate in the Taiwan area in 2016, the atmosphere corrosivity of Taiwan was generally higher than level C3, and in some coastal areas the corrosivity level was greater than level C5, reaching level C5+ (that is level CX) [7]. The best way to evaluate the durability of metal supporting devices is to place them in a known corrosivity area and to apply the field exposure test directly. The corrosion tests of various structural materials (aluminum or coated steels) used in PV structures are conducted by exposing them to the sea, and the durability of materials is periodically evaluated according to the extent of corrosion [8]. Four anti-corrosion approaches can be applied in a marine environment [9], and four different polymeric coatings on 314 SS are introduced to prevent corrosion for marine applications [10]. Nevertheless, this test method takes an enormous amount of time. To evaluate the durability of supporting devices quickly and efficiently, it is practical to artificially produce a highly corrosive environment in order to conduct salt spray tests in the lab. Numerous studies have employed salt spray tests, not only on grounding connections [11], but also on glass [12] and modules [13] in PV systems. The results demonstrate that the presence of ions (Na\(^+\), Cl\(^-\), etc.) in salt water have a much greater effect on the corrosion rate of metal connectors than in just heat and high humidity [11]. As the test conditions of an artificial environment are usually harsher than that of an atmosphere environment, the test time can be reduced dramatically [14,15]. The visual observation method, area observation method, and weight observation method are recommended to determine the degree of corrosion [16].

Figure 1. Types of floating photovoltaic (FPV) systems.
Because environmental conditions on the surface of water are harsher than on the ground; however, regulations or standards relevant to the application of supporting devices in FPV system are insufficient now [17]. Currently, it is being planned that FPV systems in Taiwan will be installed on water areas, such as reservoirs, lakes, ponds, and fish farms, and there are a lack of data about whether the supporting devices will be safe enough to endure long term use [18]. As a result, this study aims to investigate the durability of supporting devices through accelerated corrosion tests as a reference for future evaluations of the minimum requirements of supporting devices.

2. Materials and Methods

The salt spray test is an accelerated test for corrosion resistance that is not only applicable to metals and their alloys, but also to the surface coverage layer or surface modification layer, for example anodic oxide film, chemical conversion film, electrodeposit, chemical deposit, organic coating layer, and so on. The salt spray test can be categorized into three methods according to corrosivity—neutral salt spray (NSS), acetic acid salt spray (AASS), and copper-accelerated acetic acid (CASS).

In accordance with ISO 9227 [14], the NSS test consists of a neutral (pH = 6.5–7.2) 5 ± 0.5% sodium chloride (NaCl) solution delivered to a nozzle by saturated compressed air. The free falling rate of spray should be controlled within 1.5 ± 0.5 mL/h at 35 ± 2 °C. The AASS test consists of an acidic (pH = 3.1–3.3) 5 ± 0.5% NaCl solution that is tuned by an acetic acid solution, and thus the corrosion rate of AASS is faster than for NSS. The CASS test contains additional 0.0205 ± 0.0015% cuprous chloride (CuCl₂) added into the acidic (pH = 3.1–3.3) NaCl solution. Because copper ions promoted corrosion reactions to happen faster, temperatures were raised to 50 ± 2 °C, so and CASS had a faster corrosion rate than AASS. The test time was determined by the material property and test demands, and included 2, 6, 24, 48, 96, 168, 240, 480, 720, and 1008 h, or any other specific time and interruption of test time as long as it did not exceed beyond one hour each day. The differences of three salt spray test conditions are listed in Table 1.

Considering the stronger corrosivity of CASS, in this study, we preferentially utilized the CASS test because of its faster corrosion rate in order to simulate the long-term influence of corrosion for an atmospheric environment on the supporting devices on a water surface. We attempted employing a faster and more effective method to evaluate the durability of the supporting devices in the FPV system, and compared the varying corrosion extent of the supporting devices between NSS, AASS, and CASS. Generally speaking, the extent of corrosion in the one-day NSS test was equivalent to exposure to a coastal environment (level C5+) for 120 days or to a general environment (level C3) for one year. Similarly, the extent of corrosion in the one-day ASS test was equivalent to exposure to a coastal environment (level C5+) for 360 days or to a general environment (level C3) for three years.

Figure 2. (a) Corrosion of metal supports, retainers, and screws, and (b) metal corrosion and strong wind loosen solar panels.
The extent of corrosion in the one-day CASS test was equivalent to exposure to a coastal environment (C5+ level) for 960 days or to a general environment (C3 level) for eight years. It should be noted that aforementioned conversion formulas are merely empirical formulas, and the corrosion rate would be affected by the intrinsic property of metal material, the method of surface treatment, and the different deposit layers or coating layers.

| Test Method Item                  | Neutral Salt Spray (NSS) | Acetic Acid Salt Spray (ASS) | Copper-Accelerated Acetic Salt Spray (CASS) |
|----------------------------------|--------------------------|-----------------------------|--------------------------------------------|
| Temperature                      | (35 ± 2) °C              | (35 ± 2) °C                 | (50 ± 2) °C                                |
| pH (collected solution)          | (6.5–7.2)                | (3.1–3.3)                   | (3.1–3.3)                                  |
| Concentration of sodium chloride (collected solution) | (50 ± 5) g/L             |                             |                                            |
| Average collection rate for a horizontal collecting area of 80 cm² | (1.5 ± 0.5) mL/h         |                             |                                            |
| Periods of test                  | 2, 6, 24, 48, 96, 168, 240, 480, 720, and 1008 h |                             |                                            |

The ± tolerances given are the allowable operational fluctuations, which are defined as the positive and negative deviations from the setting of the sensor at the operational control set point during equilibrium conditions. This does not mean that the set value may vary by plus/minus the amount indicated from the given value.

**Table 1. Comparison table of salt spray test conditions.**

3. Results and Discussion

3.1. SUPERDYMA Shape Steel and Five Types of Screw

SUPERDYMA shape steel is a Zn-Al-Mg-Si coated steel from Nippon Steel and Sumitomo Metal in Japan, with a coating composition consisting of zinc as the main substrate in combination with aluminum (about 11%), magnesium (about 3%), and a trace amount of silicon (about 0.2%). The corrosion rate of SUPERDYMA is only one-thirtieth as fast as that of the general hot-dip galvanized steel, because the Zn-Al-Mg-Si coated layer produces a compact protection layer during the corrosion process and then contributes to the effective suppression of corrosion. A protection layer is also generated in the corrosion process of hot-dip galvanized steel, but has an inferior effect on the suppression of corrosion as a result of the lower density of the protection layer, leading to water and oxygen penetration. In contrast, Zn-Al coated steel contains 55% aluminum and thus has a stronger corrosion resistance [19]. Similar to aluminum, the ability of Zn-Al coated steel to resist acidic corrosion is superior to that of Zn-Al-Mg-Si coated steel, while its ability to resist alkali corrosion is inferior to that of general hot-dip galvanized steel [20,21]. Although the type 304 stainless steel (SS) or other higher number steels have a better acid and alkali resistance, their ability to resist chloride is weaker. Overall, Zn-Al-Mg-Si coated steel has an excellent corrosion resistance and alkali resistance, but normal acidic resistance. Furthermore, the thicker the coating layer, the better the corrosion resistance. Shape steel K27 (thickness of coating layer is 0.068 mm) was selected as the substrate on which the screws were fastened in this study. The five types of screw, from left to right, were the 304 SS screw, the 410 SS screw, the XP zinc–tin alloy coated steel screw, the galvanized steel screw capped with a type 316 SS nut, and the chromate-passivated galvanized steel screw. Each type had an equal number of screws (n = 4), including two of with an outward tail (upper row) and two with
an outward head (lower row), and a total of 20 screws without any rust had metallic luster before testing, as observed in Figure 4a.

Figure 3. Test system for the salt spray corrosion.

A white substance started to emerge on the surface of the K27 shape steel after the five-day (120 h) test, as observed in Figure 4b. This white substance was unable to be removed through washing with water. In other words, it was not a salt deposit, but the protection layer generated from the Zn-Al-Mg-Si coating dissolution during the corrosion process. Zinc hydroxide $\text{Zn(OH)}_2$ and simonkolleite $\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot\text{H}_2\text{O}$ were shown to be the materials of composition for the white substance \[22,23\]. The white protection layer was particularly obvious in the interface of the fastened screws. This can be interpreted by the fact that magnesium in Zn-Al-Mg-Si coating layer has lower standard reduction potential (anode). When in contact with other metals, such as iron, zinc, or aluminum (cathode), the magnesium corroded before the others, which led to the production of the white protective layer around the screws. The larger the reduction potential difference of the heterogeneous metals, the more easily the white protection layer generated quickly because of its strong causticity. What is more, the smaller area cathode, the larger the current density and the more severe the corrosion.

As observed in Figure 4c, after the eight-day (192 h) test, the surface of the K27 shape steel was almost completely covered by the white protection layer, but a local region was already rusted. This result indicates that most of the surface of the K27 shape steel was resistant to corrosion, while only a partial area of the white protection layer was fully corroded and rusted further into the ground layer steel. If the time for rust generation needs to be delayed, a shape steel with thicker coating layer could be employed.
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Figures 5 and 6 show the results of the five types of screws after the five-day (120 h) test and eight-day (192 h) test, respectively. As observed from the heads of the screws, both the type 316 SS nut capped on the galvanized steel screw and the type 304 SS screw presented with no rust, yet the type 304 SS screw lost its metallic luster and the other remained. On the contrary, the type 410 SS screw not only lost its metallic luster, but red rust formation was also found. These results suggest that type 316 SS (containing chromium, nickel, and molybdenum) had the highest corrosion resistance, followed by type 304 SS (containing chromium and nickel) and type 410 SS (containing chromium). In addition, a small amount of red rust was also produced on the chromate-passivated...
galvanized steel screw, and some yellow substances were found on the XP zinc–tin alloy coated steel screw instead of rust.

As observed from the tails of the screws, only little red rust as generated on the 304 SS steel screw in comparison with the 410 steel screw, which was consistent with the data that the 304 SS steel screw had a higher corrosion resistance ability than the 410 SS steel screw, as mentioned in the previous paragraph. The tail of the galvanized steel screw capped with a type 316 SS nut was a general galvanized steel screw, upon which more red rust was produced compared with the chromate-passivated galvanized steel screw. This could be attributed to the chromium-containing chemical conversion coating on the surface of the chromate-passivated galvanized steel screws, which had a better corrosion resistance than the general galvanized steel screws. Moreover, the XP zinc–tin alloy coated steel screw produced numerous yellow substances instead of red rust on the original silver white surface. We believe that those yellow substances are the protection layer resulting from the zinc–tin alloy coating layer dissolution, and not only suppress further corrosion, but also possess a strong corrosion resistance ability because of its fairly compact structure. The composition of the yellow substance was stannous hydroxide Sn(OH)$_2$ and Sn$_4$(OH)$_6$Cl$_2$ [24–27].

Last, a comparison between the heads and tails of the screws revealed that the corrosion degree of the tails of the screws was more severe than the heads of the screws. A possible explanation for this is that the coating layer or protection layer of the screws were prone to thinning and even to partial peeling when screws were used as tapping substrates, which reduced the corrosion resistance greatly. It is noteworthy that heavy wearing or peeling of the coating layer is difficult, because the coating layer of the XP zinc–tin alloy coated steel screw not only has a quite a compact structure, contributing to
a higher hardness, but also has a great adhesion with the inner steel screw. As a result, yellow protection layers were generated on the tails of the screws during corrosion, while the corrosion on the heads of the screws was not as evident as on the tails of screws. For the purpose of further investigating the corrosion resistance characteristics of the zinc-tin alloy coating layer, we performed more detailed tests separately on the XP zinc–tin alloy coated steel screw.

3.2. ALZIN XP Screws/Bolts/Nuts

ALZIN XP screws, bolts, and nuts were all covered with a zinc–tin alloy coating layer from Kwik-coat in Australia. The zinc–tin alloy with 20–30% zinc in the coating layer had the best corrosion resistance ability, and its corrosion rate was only one-tenth that of general galvanized zinc steel. In addition, the XP zinc–tin alloy coated steel screws, bolts, and nuts had an excellent machinability and weldability. Because of the strong coating layer structure with a high hardness and great adhesion between the coating layer and inner steel screw, it was not easy to wear or peel the coating layer significantly when one touched the substrate. Moreover, when the zinc–tin alloy was in contact with magnesium, aluminum, or zinc, it was less likely to cause heterogeneous metal corrosion because of the smaller difference in the reduction potential between the heterogeneous metals. With the goal of excluding the wearing or peeling of the coating layer and heterogeneous metal corrosion, we undertook a test by hanging brand-new unfastened XP zinc–tin alloy coated steel screws, bolts, and nuts directly using a fishing line.

Figures 7 and 8 show the results of XP zinc–tin alloy coated steel screws, bolts, and nuts before the test (0 h) and after the eight-day (192 h) test, respectively. Samples without any rust showed metallic luster before the test. After the eight-day CASS test, yellow
protection layers were produced at both the heads and tails of the XP zinc–tin alloy coated steel screws, and only fine dot-like red rust was found instead of the more apparent red rust. On the other hand, yellow protection layers, as well as larger dot-like red rust, were produced at the heads of the bolts, and red rust was generated at the tails of bolts as well. Likewise, red rust was produced on the outer layer of the XP zinc–tin alloy coated steel nuts.

**Figure 7.** The appearance of an XP zinc–tin alloy coated steel screw/bolt/nut before the CASS test (0 h): (a) screw head, (b) screw tail, (c) bolt head, (d) bolt tail, and (e) nut.

We inferred from the results in the previous paragraph that the zinc–tin alloy coating layer would initially be dissolved in order to generate the yellow protection layer to suppress corrosion. If corrosion happened continuously, a lot of red rust would be produced due to a depletion in the zinc–tin alloy coating layer, leading to further corrosion of the inner steel. Furthermore, the results of the eight-day CASS test in the method of hanging the XP zinc–tin alloy coated steel screws by a fishing line appeared to be more significant than for the method of fastening XP zinc–tin alloy coated steel screws on the Zn-Al-Mg-Si coated steel. Not only were yellow protection layers produced at the tails of the screws, but yellow protection layers and dot-like red rust were produced at the heads of the screws as well. Because the unfastened XP zinc–tin alloy coated steel screws hung by a fishing line were brand-new, factors of wearing and peeling of coating layers or heterogeneous metal corrosion could be excluded. A possible explanation for this is that the zinc–tin coating layer had a worse acidic corrosion resistance. Although the CASS test was performed for only eight days (equivalent to 64-day NSS test according to empirical formulas), more significant consequences of corrosion were observed compared with the 136-day NSS test, as observed in Figure 9. Many papers have discussed about the comparison of corrosion behavior between NSS and field exposure test. The results showed that the extent of corrosion in the NSS test is more severe than for the field exposure test [28,29]. Therefore, the CASS test is certainly a faster and more efficient accelerated corrosion method than the NSS and field exposure tests.
4. Conclusions

The visual observation of five types of screw fastened in SUPERDYMA shape steel using the CASS test has demonstrated that the surface of SUPERDYMA shape steel was almost completely covered by a white protective layer, but a local region had already rusted. This result indicates that most of the surface of the SUPERDYMA shape steel was resisted corrosion, while only a partial area of the white protection layer was fully corroded and further rusted into the ground layer steel. We observed the heads and tails of five types of screws with varying degrees of rust. Type 316 SS had the highest corrosion resistance, followed by type 304 SS and type 410 SS. The chromate-passivated galvanized steel screw had a better corrosion resistance than the general galvanized steel screw because of the contribution of a chromium-containing chemical conversion coating. The XP zinc–tin alloy...
coated steel screw produced numerous yellow protection layers instead of red rust to prevent further corrosion. Furthermore, the corrosion results of the XP zinc–tin alloy coated steel screw and galvanized steel screw capped with a 316 SS nut revealed that the corrosion degree of the eight-day CASS test was more significant than that of the 136-day NSS test. Therefore, the CASS test is a faster and more efficient method for evaluating the durability of the supporting devices. It is an accelerated corrosion method that needs more research, for example through a comparison of the corrosion weight loss, corrosion potential, and potentiodynamic polarization parameters between the CASS test, NSS test, cyclic corrosion test (CCT), and field exposure test.

Environmental conditions on the surface of water are harsher than on the ground; however, regulations and standards relevant to the application of supporting devices in FPV systems are currently insufficient. Users can only rely on the test data provided from manufacturers or agents to estimate the lifetime of supporting devices, or unilaterally believe the uncertified warranty of supporting devices that manufacturers or agents provide. Currently, FPV systems in Taiwan are planned to be installed on water areas, such as reservoirs, lakes, and fish farms, and there are a lack of data to evidence whether the supporting devices are safe enough to use enduringly. As consequence, both the safety and durability of supporting devices in FPV systems are urgent issues that need to be resolved if a government is planning on positively implementing green energy and installing FPV widely. Standard test methods for supporting devices in FPV systems must be established as soon as possible, and the minimum requirements of supporting devices must be evaluated in order to enhance the minimum service life further, reduce the risk of damage to supporting devices, and reduce the overall maintenance costs.

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