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Electrochemical Impedance Spectroscopy (EIS) Study of Coconut Water as Natural Inhibitor in Malay Traditional Preservation of Iron Artefact

M.Musa¹, Hadi Purwanto¹, R. Razak³, R.Othman², Luqman Musa⁵ and MH Ani¹

¹Department of Manufacturing and Materials Engineering, Kulliyah of Engineering, International Islamic University Malaysia, Gombak, Selangor, Malaysia.

²Department of Sciences in Engineering, Kulliyah of Engineering, International Islamic University Malaysia, Gombak, Selangor, Malaysia.

³Applied Arts and Design, Kulliyah of Engineering, International Islamic University Malaysia, Gombak, Selangor, Malaysia.

⁴Institute of Microengineering and Nanoelectrics, Universiti Kebangsaan Malaysia (UKM), 43600 Bangi, Malaysia

⁵Centre of Excellence Geopolymer and Green Technology (CEGeoGTech), School of Materials Engineering, Universiti Malaysia Perlis (UniMAP), Perlis

Email: mhanafi@iium.edu.my

Abstract. Treating and cleaning corroded artefact has resulted in long-term loss of artefact integrity and intangible historical value in museum preservation method. Inhibitors and coatings are preferable methods applied in heritage conservation as it is the easiest way for corrosion protection. However, issue of health and environment has led conservators to find a better inhibitor, natural or green corrosion inhibitors. Surprisingly, Malay traditional practice has since long ago used Coconut water (CW) as corrosion inhibitor to preserve keris blades, showing that the knowledge in corrosion protection has been practiced in old Malay civilization for metal preservation. This paper intends to clarify the compositional effect of CW in the inhibition efficiency to iron-based keris blade. Through Tafel and Electrochemical Impedance Spectroscopy (EIS) and Energy dispersive analysis of X-rays (EDAX) analysis, the study showed that CW formed passivation with the highest IE of 92% as compared to other natural inhibitors existing and used in industries such as Ascorbic Acid (AA) and Tartaric acid (TA). EIS and Scanning Electron Microscope (SEM) study has shown and conclude that CW has displayed protective abilities that exceeds both AA and TA.

1. Introduction

Continuous cycle of corrosion followed by treating and cleaning corroded artefact has resulted in long-term loss of artefact integrity and intangible historical value [1]. Performing indoor environmental control with equipment to protect artefact from corroding is easy but costly to most museums [2]. Due to this reason, inhibitors and coatings are preferable methods applied in heritage conservation [3]. However, inhibitors used in heritage preservation are borrowed from industries and not specifically used in heritage preservation usage and some claims that it is even hazardous [4]. This led conservators to extend the search for safer and environmentally-friendly compounds, Green Corrosion Inhibitor (GCI) in metallic artefacts [5]. Eventhough both inhibitors, tannic acid and Benzotriazole



(BTA) were preferred in archaeological iron artefact [6], but little study has been done on iron historical artefacts [7]. There are several natural inhibitors extracted from natural resources used in industrial and give a good result, such as *Garcinia Mongastana pericarp* which give highest inhibition efficiency with 98% [8]. In Malay traditional practice keris preservation, coconut water (CW) is used as inhibitors. It is used to protect keris blade, an iron based as early as keris fabrication was explored. Surprisingly, Coconut water give a value of 93% inhibition efficiency for industrial application [9]. Several organic acid and inorganic ions are present in CW water, such as ascorbic acid, tartaric acid and malic acid [10]. Some of composition in CW is similar to organic inhibitor used in industries. However, there are no empirical study been conducted to analyse the functional CW and its relation to corrosion protection of keris blade. Hence, this paper intends to clarify the compositional effect of CW in the inhibition efficiency to iron based keris blade.

2. Methodology

2.1. Materials and Sample Preparation

Study on corrosion behaviour was conducted by employing Tafel analysis and Electrochemical Impedance Spectroscopy (EIS) and surface observation. The gravimetric test (weight gain) also was carried out to support the Tafel and EIS experiment. Samples for weight gain and Tafel as well as for Electrochemical Impedance Spectroscopy (EIS) analysis were prepared from prepared keris blade with main composition is 95.7% Fe and 2.99% steel. Samples were cut cross-sectional from keris blade into size (1 x 1 x 0.5 cm) and abraded with wet SiC paper from 800 till 2000 grades and polished with Al₂O₃ paste from 1 to 0.01 μ m to get mirror-like polish. Organic acids; Ascorbic acid (AA), Tartaric Acid (TA) and Malic Acid (MA) used were from Sigma Aldrich brand with purity above 90%. These organic acids were selected as inhibitors in this experiment due to the fact that they were used in industries and they are major organic acid present in CW as reported by Jean W.H. Yong, Liya Ge, Yan Fei Ng and Swee Ngin Tan,(2009).

2.2. Corrosion Analysis

Initial weight and after immersion into respective solution were recorded precisely for calculation of weight gain. Samples were completely immersed for 1,3,5 and 7 days, followed the traditional keris upkeep. Hundred samples were used in Tafel and EIS analysis, which 10 samples for each electrolyte in Tafel and Electrochemical Impedance Spectroscopy (EIS) analysis. Tafel and Electrochemical Impedance Spectroscopy (EIS) analysis was conducted by using a Metro Ohm Autolab PGSTAT320N. In Potentiodynamic polarisation analysis, samples were used as working electrode (WE) while Reference Electrode (RE), Ag/Ag-Cl was used and adjusted about 1mm adjacent to the WE Counter electrode which used Platinum wire. The measurements were performed at a potential scanning rate of 10 mV/min. The potential range was from -200 mV to 200 mV and immersed in electrolyte 10 cyclic in 2 minutes. In EIS study, an AC amplitude of 10 mV was applied in measurement with the frequency ranged between 100 kHz to 100 mHz using 5 points per decade. The EIS parameters were obtained by fitting the experimental results to an appropriate equivalent circuit. The impedance spectra measurements were carried several ways, by immediate immersion and after 4 hours of exposure to the WE in the solutions. Then results were recorded immediately. Another study carried out was surface morphology observation SEM-EDAX after samples were immersed in solution for Tafel and EIS analysis.

3. Results and Discussion

3.1. Gravimetric Test

It is interesting to note that sample in coconut water has the lowest mass gain, while the sample in ASTM water has the highest mass gain. During the initial period (less than 3 days), all samples show

linear increase of the mass gain except sample in a tartaric acid. This particular sample resulted in a plateau-shaped plot of the mass gain as shown in figure 1. After 5 days, all samples displayed the same plateau-shaped mass gain thus signifying that the oxide film has reached enough thickness and further corrosion is controlled by solid diffusion of ions in the oxide film. As additional result, a combination of TA and AA (TAAA) is also used immersion for the blade. It is observed that between 3-5 days, the weight gain of the samples in a mixture of tartaric and ascorbic acid (TAAA) overtakes the sample in ascorbic acid. Since the weight gain of sample in tartaric acid is always higher than coconut water, ascorbic acid, and TAAA, it is deduced that the chemical substance in TA somehow accelerates the corrosion rate. However, since TA is a substance of CW, some other trace elements or substances such as minerals in CW may also potentially prevent further corrosion in CW.

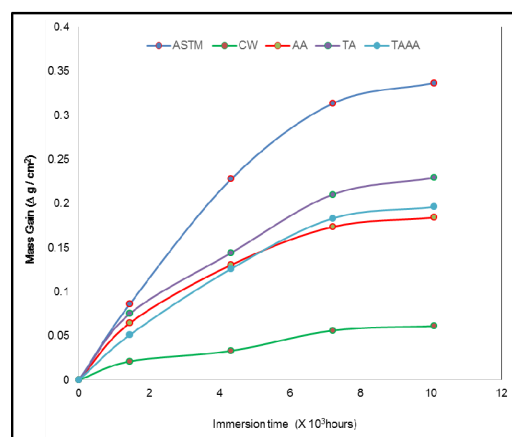


Figure 1. Graph of mass different after immersed in different inhibitors.

3.2. Tafel Analysis

The effect of corrosion protection in ASTM water was observed and evaluated from figure 2.. Result shows that potential of sample by addition of CW had shift markedly to the negative side in comparison to other samples. Current plateau was observed in CW at the range of -0.8 to -0.25 V, showing passivation characters presence in CW which contradicts other inhibitors.

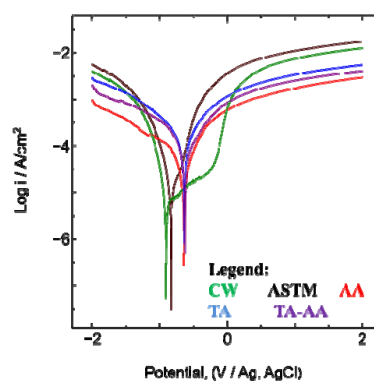


Figure 2. -V plot of Keris blade in CW, AA, TA and mixture Tartaric Acid and Ascorbic Acid (TA-AA).

Further investigation was carried out from Tafel study and tabulated in table 1 where has shown that the IE of CW is the highest compared to other inhibitors by 20% better than AA and 54% better than TAAA, This shows that the TA and AA are not only organic acid that contributes to a better IE in CW. There are other factors and composition that could contribute to the result and therefore further studies need to be conducted.

Table 1. Corrosion parameters in various inhibitors determined by Tafel extrapolation method.

	E_{corr} mV	$b_a, \text{mV.dec}^{-1}$	$b_c, \text{mV.dec}^{-1}$	i_{corr} μAcm^{-2}	Corrosion rate (mm^{-1})	Inhibition Efficiency, IE (%)
CW	-895	-143	-1844	7.42×10^{-6}	6.28×10^{-2}	92
AA	-641	-264	-268	2.37×10^{-5}	2.00×10^{-1}	74
TA	-643	-288	-397	7.97×10^{-5}	6.74×10^{-1}	15
TAAA	-642	-226	-209	5.43×10^{-5}	4.59×10^{-1}	42
ASTM	-497	-242	-490	9.42×10^{-5}	7.96×10^{-1}	-

3.3. Electrochemical Impedance Spectroscopy (EIS) Analysis

Generally, coatings are reported to have an equivalent circuit model of R(C[R(CR)]) as shown in figure 3a [11]. However, certain instances another model is required to explain the resulting impedance spectra. For example, metals with phosphate coating have a different circuit model shown in figure 3b [12]. CW-treated samples in this study were tested for its corrosion resistance against several other prepared organic coatings. It needs to be noted that CW contain a mixture of mildly major organic component and relatively large amounts of inorganic compound, phosphorus and manganese in addition to its various compounds.

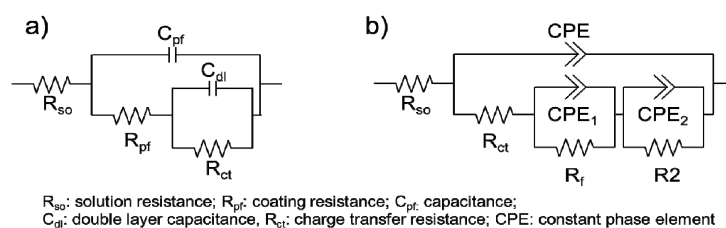


Figure 3. (a) Equivalent circuit model of defective organic coated metals as generally reported in the literature [11] (b) Equivalent circuit model for coated steel [13]

Identifying the active compounds responsible for its corrosion protection abilities would be quite hard. However, it might be useful to consider the compounds in terms of whether it is inorganic or organic (for the aforementioned compounds), which has various reports on EIS characteristics of metal with coating. This was done through evaluating the chi-squared values of each equivalent electrical circuit (EEC) model fitted to the impedance data to find a suitable one. It could be hypothesized that treatment with coconut water also produced a coating similar to the manganese phosphor coating used industrially. As mentioned in 2.1, CW also has relatively large amount of inorganic compound and therefore an EEC reported for phosphate coatings and other common EEC were tried and compared to models with organic coating and fittings as shown in figure 4. It can be immediately concluded that

circuit **E** has very large deviation, and **G** which has large chi-squared value is not the suitable model. In contrast to these, circuit **A** seems to provide the best fit. Since $\alpha < 1$, this either suggests some form of surface heterogeneity or diffusion process occurred during EIS.

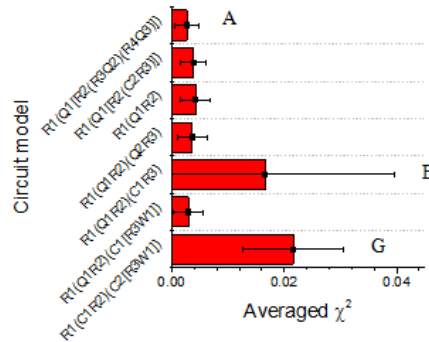


Figure 4. EIS circuit fitting for each model compared by averaged χ^2 value of all treatments of AA, TA, CW and blank.

EIS circuit in this study is fitting for each model compared by averaged χ^2 value of all treatments of AA, TA, CW and blank. narrowed our focus on circuits R(RQ)(RQ), R(QR)(C[RW]), and R(Q[R(RQ)(RQ)]) which provide the best average fit. Values for each element are plotted in figure 5. Circuit element values for an EEC shown in figure 5 (a & b) are commonly related to organic coatings, whereas Figure 6 c shows fitting from an EEC reported for inorganic coating. R1 for all EEC for each coating including those not plotted here, gives a value of about 500 Ω . This value represents bulk solution resistance of the ASTM water. While EECs for organic coating (figure 5 a & b) present a good fit, Figure 5 b provides a better fit with its Warburg diffusion element or Warburg impedance, W. Warburg impedance is a measure of difficulty of diffusion caused by any Faradaic process. Relating this to the observation made in figure 5, it can be seen why a capacitor element gives a bad fit.

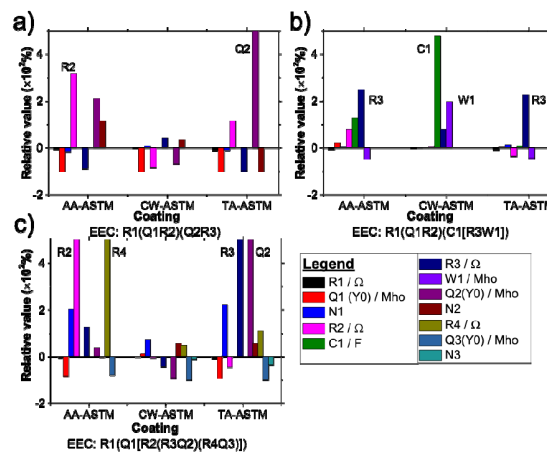


Figure 5. Normalized values for each circuit elements from various EEC for each. Values are normalized against blank data (ASTM Water)

A truly protected metal would only have double layer charging, a non-Faradaic process, making it similar to a capacitor. However, incomplete/defective coating has corrosion process, a Faradaic process, thus requiring constant phase and Warburg elements to explain its mechanism. Resistance values from EEC circuit $R(Q[R(RQ)(RQ)])$ displays an anomaly where resistance R_3 and R_4 reaching $1 \times 10^{12} \Omega$ which is the maximum allowed limit in the EIS software (figure 5c). These anomalies (while not necessarily bad) occur when only a coating of organic acid (tartaric acid and ascorbic acid) was used. In fact, this particular EEC was the reported circuit for an inorganic coating created from phosphate conversion coating.

This results in a possible incompatibility towards metal substrates with organic coating. Considering the exceptionally good fit of this circuit, there is a possibility of an inorganic phosphate-manganese coating being present on the metal surface as well. Elemental analysis will prove the presence of the concerned elements of this coating.

Comparing values for Warburg elements in $R(QR)(C[RW])$, metals treated with organic coating has the lowest value of 0.0067 Mho and 0.0068 Mho for each AA and TA-coated metal, as seen from figure 6. Coconut water (CW) treatment gives the highest Warburg value of 0.0370 Mho suggesting a bigger barrier in the corrosion process. Furthermore, from R_2+R_3 which is corrosion resistance, only ascorbic acid and coconut water shows an improvement against the blank sample. In fact, only coconut water treatment consistently shows improvement against the blank sample. On the other hand, tartaric acid has little to no protective abilities from this EIS which data from Tafel also agrees. It is believed that this is caused by its extremely high pKa values of 3.2 and 4.8 as compared to ascorbic acid which has 4.1 and 11.8 where its acidity overcomes any of its protective abilities.

EIS analysis has provided several important information on the coating formed on the metal surface. Several EEC were tested for metal substrates treated with AA, TA and CW. $R(QR)(C[RW])$ was found to have the best fit for all treatment methods but according to χ^2 value, there is a possibility of both organic and inorganic coating being formed on the metal surface. However, the coatings produced using current preparation methods are not completely protective but coconut water displays protective abilities that exceeds both ascorbic acid and tartaric acid. Longer immersion times or several repetitions of coconut water immersions could be expected to produce better results. Also, the possibility of the formation of inorganic coating from coconut water might be an interesting avenue to explore in the future.

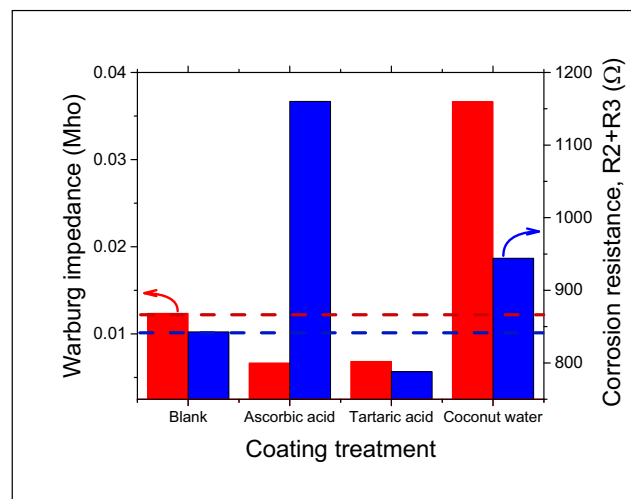


Figure 6. Comparison of $R(QR)(C[RW])$ circuit elements of Warburg impedance, W and corrosion resistance, R_2+R_3 .

3.4. Film Formation and Characterization

Further investigation on film formation was carried out using SEM-EDAX. Figure 7 shows the morphology of sample surface after being immersed in respective electrolyte. Sample with CW had the most flat film with large grain size and crack as compared to sample in TA, it shows a large crack of oxide film with substrate below the film is heavily attached by TA. This explains why the sample in TA is having greater corrosion rate compared to CW and AA.

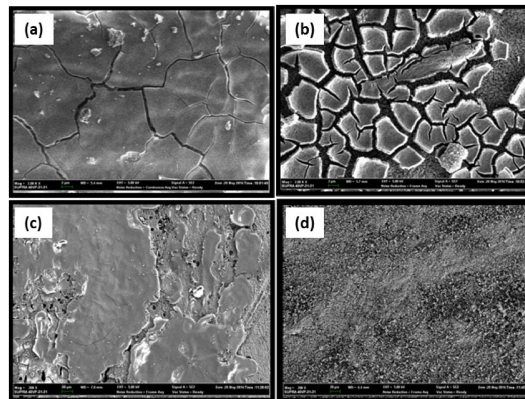


Figure 7. SEM- EDAX (magnification X1000) of passivation sample immersed in (a) CW (b) AA (c) TA and (d) ASTM for 5 days.

EDX result of element composition of oxide film formed on keris blade after immersion in particular solution is shown in table 4. This due to that sample immersed in CW has a similarity composition of film formation with composition in CW as shown in table 2.

Table 2. Presence of element in immersed keris blade.

Sample	C	O	Cl	P	S	Mn	Fe	Total
CW	22.43	38.33	2.25	0.72	0.60	11.76	23.91	100.00
AA	5.31	60.97	0.00	0.00	0.00	0.99	32.73	100.00
TA	6.83	62.69	0.00	0.00	0.00	0.75	29.83	100.00
ASTM	1.76	35.79	0.00	0.00	0.00	0.00	62.45	100.00

Sample immersed in ASTM water shows high percentage of Fe and O which demonstrated the formation of iron oxide, while sample immersed in CW shows high percentage of Mn, O and C which simplify the formation of manganese oxide. This explains the film crack out, due to low stress tolerance of manganese oxide. Both samples immersed in TA and AA show similar results when compared with CW except having high percentage of O but lower percentage of Mn and C. This could explain why AA and TA having a close effect in result of corrosion protection in compared to CW.

Conclusions

Corrosion behaviour of keris blade in various CW and it acidic substance were evaluated and can be concluded as follows:

1. Through Tafel analysis it is obviously shows that CW has formed passivation characters, having the IE of 92%, which is in agreement of previous study [Abiola, O. K. and Tobun, Y.,2010].
2. Coconut water treatment consistently shows improvement against the blank sample. This can be seen from EIS analysis. It was also found that R(QR)(C[RW]) is the best fit for all treatment

methods. However, due to χ^2 value, there is a possibility of both organic and inorganic coating being formed on the metal surface.

3. Coconut water has displayed protective abilities that exceeds both ascorbic acid and tartaric acid. Longer immersion times or several repetitions of coconut water immersions could be expected to produce better results. Sample with CW had the most flat film with large grain size and crack. Compared to samples in CW and AA, sample in TA showed a large crack of oxide film with substrate below the film is heavily attached by TA. This explains why the sample in TA is having greater corrosion rate compared to CW and AA.

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