

Impact of AC Anodizing on SS304L Oxide Film and Its Effect on Hydrogen Evolution Reaction (HER) Properties

Nur Suhaily Azmi¹, Mohd Nazree Derman^{1,2,*} and Zuraidawani Che Daud^{1,2}

¹Faculty of Mechanical Engineering & Technology, Universiti Malaysia Perlis, Perlis, Malaysia

²Frontier Materials Research, Centre of Excellence (FrontMate), Universiti Malaysia Perlis, Perlis, Malaysia

ABSTRACT

The effect of AC anodizing on the formation of oxide film on stainless steel 304L (SS304L) surfaces and its influence on the hydrogen evolution reaction (HER) were studied in this study. The SS304L specimens were prepared before being anodized for 30 minutes at various voltages (range from 10 V to 50 V) using an AC power supply at room temperature. The surface morphology is studied using scanning electron microscope (SEM) and 3D profilometer. A potentiostat is used to run linear sweep voltammetry (LSV) and Tafel analysis for the HER characterization. The result recorded the highest thickness of 9273.45 nm at 40 V anodizing voltage and the lowest surface roughness of 837.16 nm recorded at 50 V. The linear sweep polarization test solution exhibited the lowest overpotential at 50 V, 398.3 mV and a Tafel slope of 196 mVdec⁻¹. These findings provide insight on the possibility of AC anodizing for improving the surface characteristics of SS304L for use in energy conversion applications.

Keywords: AC Anodizing, Stainless Steel, Oxide Film, Hydrogen Evolution Reaction

1. INTRODUCTION

As a pollution-free, clean energy source, hydrogen has been praised as a possible replacement for the depleting and hazardous fossil fuels [1,2]. The oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER), two separate half processes, are involved in electrochemical water splitting, an innovative technique for producing high-purity hydrogen [3]. Due to the sluggish kinetics of both HER and OER, there is a need to achieve superior efficiency in electrochemical water splitting [4]. A catalyst could be used in order to overcome the problems. Commercial catalysts like ruthenium/iridium dioxide for OER and platinum for HER are used to a certain extent due to their high prices and scarcity, which highlights the need for bifunctional, highly active, and stable catalysts [5]. As a result, there has been increased interest in transition metal compounds (TMCs) [6], notably transition metal nitrides (TMNs), which have improved catalytic activity and are hence promising options for water splitting. These compounds may have their electrical structure, morphology, and active sites changed, which opens up possibilities for changing their catalytic performance [7], emphasising the need of careful consideration in the development of catalysts.

Stainless steel (SS), the most prevalent and economical alloy composed of Ni, Fe, and Cr, has gained popularity as an alternative material for energy storage and electrocatalysis due to its outstanding conductivity and durability [8]. However, a scarcity of active sites as well as the surface overpotential have prevented its direct application as a water splitting catalyst. Controlling SS's composition and electrical structure has helped enhance its catalytic activity.

* Corresponding authors: nazree@unimap.edu.my

For instance, Anantharaj and colleagues enhanced electrocatalytic performance by hydrothermally eliminating Cr from the surface of 316 SS [9]. The introduction of AC anodizing as a technique for surface modification provides a practical solution to improve the HER characteristics of SS304L stainless steel. During AC anodizing, controlled modifications to the oxide film's surface morphology, composition, and structure may result in increased electrocatalytic activity. This approach offers customized enhancements in catalytic performance, which represents an important progress towards realizing SS304L's full potential for hydrogen evolution.

2. MATERIAL AND METHODS

2.1 Sample Preparation

Table 1 presents the chemical composition of the stainless steel (SS) 304L used in this study. The SS304L samples with thickness of 2 mm were cut into sizes of 25 mm x 15 mm and undergo sample preparation of grinding, polishing and austenitizing at a temperature of 700 °C with a heating rate of 2 °C per minute. The sample surfaces were then covered with electroplating tape to ensure that just 10 mm × 10 mm are exposed during the anodizing process.

Table 1 The chemical composition of SS304L

Fe	Cr	Ni	Mn	Si	C	P	S
Balance	18.0-20.0	8.0-12.0	≤2.0	≤0.75	≤0.03	≤0.045	≤0.03

2.2 AC Anodization Process

The anodizing is a method used to create an oxide film on the surface of metal alloy. In this study, a basic anodizing setup with two electrode (anode and cathode) is used. The SS304L is set as both anode and cathode and an AC power supply as the power source. The anodizing process is carried out using voltage ranging of 10 V to 50 V in an ethylene glycol solution consist of 0.3 M ammonium fluoride, NH₄F and 3% water, H₂O. The use of anodizing voltage lower than 10 V resulting in prolong anodizing time which more than 30 minutes. This may due to thickness of SS304L used which is 2 mm. The temperature of the electrolyte is fixed at room temperature and the process is carried out for 30 minutes.

2.3 Material Characterization

A scanning electron microscope and a 3D profilometer are both used for material characterization. The surface morphology of the oxide film that has formed on the surface of SS304L is examined using the SEM model JEOL JSM-6460-L. The magnification is adjusted at 1000 times to allow for comprehensive observation of the oxide film. The 3D profilometer is used to characterize the thickness and surface roughness of deposited oxide films. As for the thickness of oxide film formed, the increment of oxide film is measured using the 3D profilometer where comparisons are made between anodized area and un-anodized area. An optical 3D profilometer is used where it directs light to capture a three-dimensional image of the surface, creating a three-dimensional output.

2.4 Electrochemical Characterization

As for electrochemical characterization, a linear sweep voltammetry (LSV) is used to study the HER activities. The characterization is carried out using an AUTOLAB PGSTAT 204 and a NOVA software. A three-electrode cell setup is used to conduct the experiment in a 1.0 M potassium hydroxide (KOH) solution. The samples are designed with a 1 cm² exposed surface area. The AC anodized SS304L serves as the working electrode whereas the counter electrode is set as platinum electrode. The saturated calomel electrode (SCE) is used as the reference electrode. The overpotential values are the main focus of the HER activity tests, with the voltage range is set between -1.65 V and -1.0 V and a scan rate of 0.01 Vms⁻¹ and Tafel analysis is measured at the same scanning speed. The formula $\eta = b \log j + a$, where η , b , and j represent the overpotential, Tafel slope, and current density, respectively, was used to calculate the Tafel slope. The equation (1) was used to refer all potential values to the reversible hydrogen electrode (RHE).

$$E_{\text{RHE}} = E_{\text{SCE}} + 0.244 + 0.0591\text{pH} \quad (1)$$

3. RESULTS AND DISCUSSION

3.1 Morphology of Oxide Film

Figure 1 reveals the differences in the morphology of the oxide film on the surface of SS304L formed by the AC anodizing process carried out at various anodizing voltages, ranging from 10 V to 50 V. Each voltage setting exhibits distinctive morphological characteristics that emphasise how the anodizing voltage affected the final oxide film. When compared to anodizing voltages between 20 V and 40 V, which are shown in Figure 1 (a), the oxide film's covering on the surface appears insufficient at 10 V. In contrast to the film created at 30 V, which has a more compact and dense structure, the oxide film formed at 20 V stands out for having a porous structure with observable gaps. The occurrence of structural properties suggests a relationship between the anodizing voltage and the phase of oxide film production, where higher voltages support further developed phases of film growth.

The oxide film reached its best level of compactness over the range of anodizing voltages investigated, as shown in Figure 1(d), at an anodizing voltage of 40 V. The oxide film develops a well-formed, compact form at this voltage, which indicates excellent anodization conditions. However, a significant difference appears after the anodizing voltage is increased to 50 V. As seen in Figure 1(e), the oxide film begins to show signs of separation and peeling off the surface of SS304L, eventually leading to a fragmented structure. The decrease of adhesion between the oxide film and the SS304L substrate might be attributed on the occurrences. This is consistent with research by Lin and colleagues [10], who found that a high anodizing voltage could damage the bond between the oxide film and the substrate below, making the film more prone to separation.

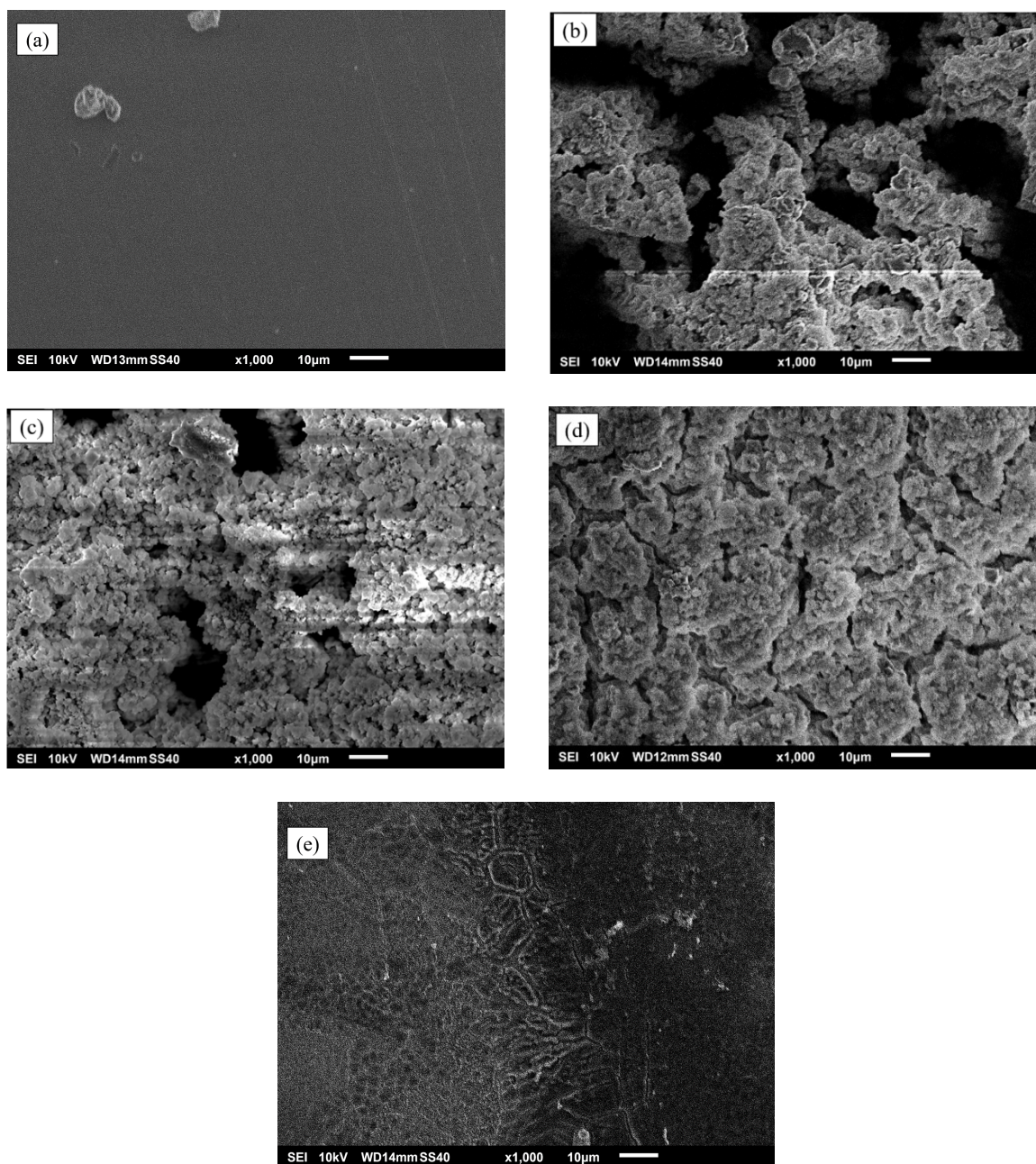


Figure 1. The SEM of oxide film formed on SS304L surface at different anodizing voltage ranging from (a) 10 V, (b) 20 V, (c) 30 V, (d) 40 V and (e) 50 V.

3.2 Surface Roughness and Thickness of Oxide Film

The surface roughness and thickness of oxide film formed on the SS304L after anodizing process at different voltage value are tabulated in Table 1 and depicted in Figure 2. The surface roughness of 104.24 nm at an anodizing voltage of 10 V indicates the early stages of oxide film development, as shown in Figure 2(a). At 20 V, the surface roughness measurement with the highest value is 2465.58 nm. This rise is explained by the development of the oxide coating on the surface of the SS304L as a result of anodic dissolution [11]. The process of oxide film production follows a sequence in which anodic dissolution occurs prior to the development of the oxide film. This continuous process causes the formation of surface characteristics, which contributes to the roughness that is actually observed.

The surface roughness continuously reduces from 1404.44 nm to 1239.01 nm as the anodizing voltage rises from 30 V to 40 V. This trend indicates the oxide film's gradually covering of the SS304L surface, leading to a more compact and uniform structure. Figure 2 (c) and (d) show the shift clearly, since the oxide coating appears compact. The measured surface roughness at anodizing voltage of 50 V is 837.16 nm. This decrease in roughness is a result of the oxide coating peeling off, a phenomenon that was previously noted. This observation is a direct outcome of the peel-off process, and the information acquired gives an understanding of the state of the SS304L surface.

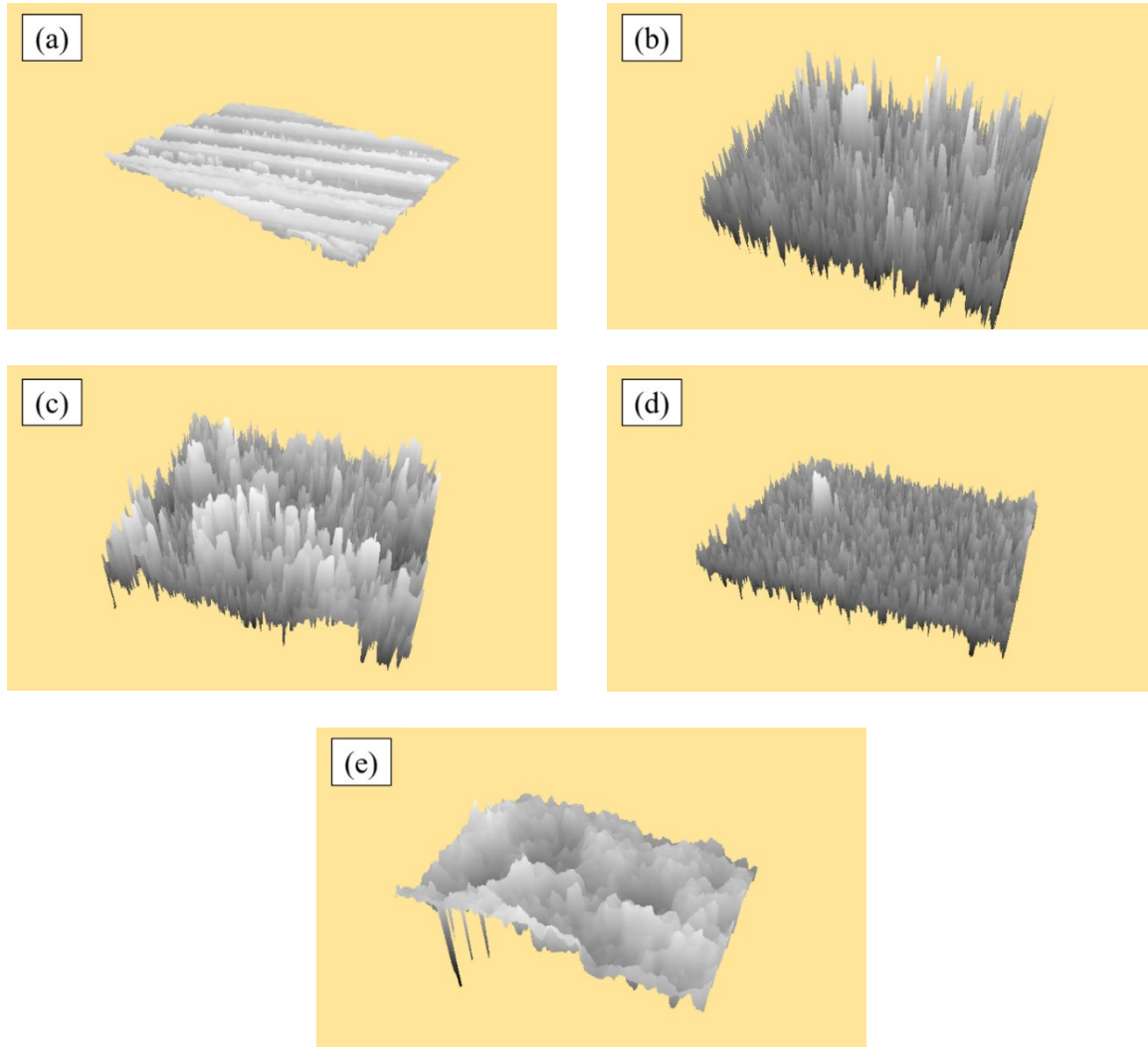


Figure 2. The 3D profilometer images of surface roughness of the oxide film formed on SS304L surface at anodizing voltage of (a) 10 V, (b) 20 V, (c) 30 V, (d) 40 V and (e) 50 V.

A noticeable trend can be seen in the oxide film thickness that results from the AC anodizing process on SS304L, with thickness values showing an ascending trend from 10 V to 40 V and a descending trend at a 50 V anodizing voltage as tabulated in Table 2. The measured oxide film thickness is 1421.88 nm at 10 V and increases noticeably to 5960.02 nm at 20 V. Measurements at 30 V and 40 V at 7245.38 nm and 9273.45 nm, respectively, indicate the trend of increasing thickness is still present. According to this formation, the amount of energy source is optimised at a 40 V anodizing voltage, producing the maximum oxide film thickness when compared to the other anodizing voltages [12]. However, at 50 V, a significant reduction in thickness is seen, diverting from the rising trend. This decline is consistent with the trends shown in the surface roughness data and can be related to the phenomena of oxide film detachment or peeling.

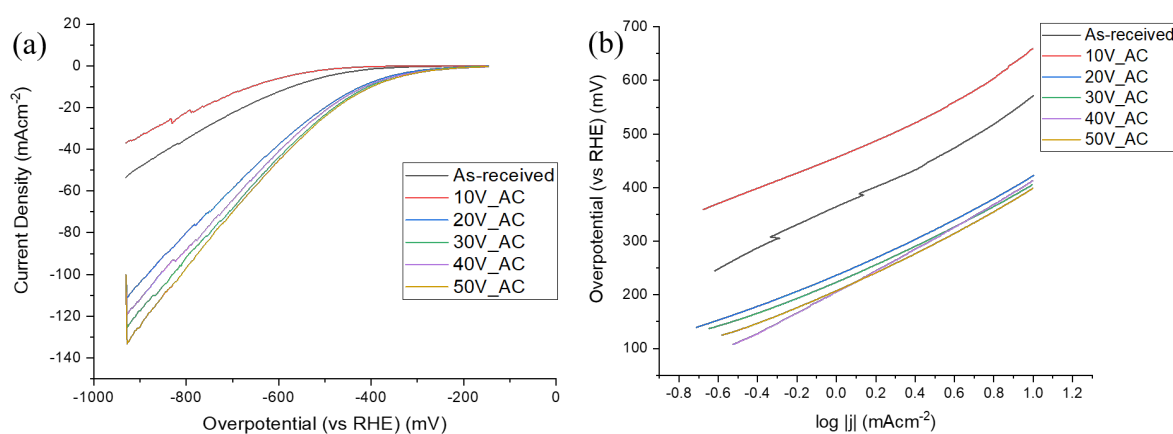
Table 2 Surface roughness and thickness of oxide film formed on the SS304L after undergo anodizing process

Voltage (V)	Surface Roughness, Ra (nm)	Thickness, t (nm)
10	104.24	1421.88
20	2465.58	5960.02
30	1404.44	7245.38
40	1239.01	9273.45
50	837.16	4009.67

3.3 HER Activities

Figure 3 (a) and (b) depicted the linear sweep voltammetry (LSV) curves and Tafel plot of the hydrogen evolution reaction (HER) properties of the as-received and AC anodized SS304L, respectively. An in-depth investigation of the HER properties is accomplished using the as-received sample as a baseline. At a current density of 10 mAcm⁻², the as-received specimen showed an overpotential of 569.2 mV. In order to better understand how AC anodizing impact on the HER properties, this value is used as a starting point for comparison with AC anodized specimens. There is a noticeable change in the HER overpotential after applying AC anodization at various anodizing voltages.

The HER overpotential significantly rises to 657.09 mV at a 10 V anodizing voltage. This change might be explained by the fact that the oxide layer on the SS304L surface may not have fully grown at 10 V, which is a rather early stage of oxide film production. The observed rise in overpotential might be caused by the presence of a less developed oxide coating. Surprisingly, at a 20 V anodizing voltage, the HER overpotential reduces to 420.7 mV. This decline demonstrates how AC anodization could improve the electrocatalytic performance of SS304L for the HER [4]. At anodizing voltages of 30 V and 40 V, respectively, the HER overpotential reaches 412.95 mV and 406.53 mV, maintaining to decrease. This gradual decrease emphasises how higher anodizing voltages improve catalytic efficiency. The most exciting result may be seen at a 50 V anodizing voltage, when a 398.3 mV HER overpotential is approximately achieved. This outcome denotes an electrocatalytic behaviour that has been optimised using AC anodization. The information supports the idea that precise control of anodizing settings can produce surfaces with increased electrocatalytic performance.

**Figure 2.** The HER properties of as-received and AC anodized SS304L specimens based on the (a) LSV curves and (b) Tafel plots.

Tafel analysis is a crucial method for evaluating electrocatalysts, notably in the context of water electrolysis. To understand the fundamental characteristics of the AC anodized SS304L as an electrocatalyst, the hydrogen evolution reaction (HER) mechanism is examined using Tafel analysis. In this work, Tafel slope analysis is the main focus since it is a crucial instrument and the Tafel slope frequently indicates the underlying HER mechanism at the particular electrocatalytic interface [9]. The Tafel slope, measured in millivolts per decade (mVdec^{-1}), offers knowledge on the HER process' rate-determining phases. Faster reaction rates are shown by a lower Tafel slope, which points to increased electrocatalytic activity. On the other hand, a higher value Tafel slope can indicate slow kinetics.

The as-received SS304L is used as a baseline for comparison in this investigation because it has the highest value Tafel slope among the AC anodised specimens, $200.22 \text{ mVdec}^{-1}$. This finding shows that the as-received specimens has significantly slower HER kinetics. As the anodizing voltage rises to 50 V, a trend develops. The Tafel slope drops steadily until it reaches 196 mVdec^{-1} . This improvement in HER kinetics, which is indicated by a decrease value in the Tafel slope, points to better electrocatalytic performance at the electrode-electrolyte interface.

4. CONCLUSION

The research investigated the many correlations between the SS304L stainless steel's HER properties, oxide film shape, and AC anodizing voltage. An important focus of the work is how the anodizing voltage affects how the oxide film appears on the surface of SS304L. The findings of these studies highlight the contradictory nature of higher voltages, which might produce compact, well-structured films but also call for cautious attention due to potential adhesion concerns. Lower voltages, on the other hand, result in films that are either inadequate or incomplete. In terms of surface roughness and thickness of the produced oxide film, the information provided highlights the importance of a 50 V anodizing voltage. Surface roughness and thickness show increasing trends with increasing anodizing voltages until this voltage value, which acts as a critical turning point, begins to significantly reduce. This fascinating behaviour emphasises the complex relationships that control the production of oxide films. The study on electrocatalytic behaviour using Linear Sweep Voltammetry (LSV) curves and Tafel slope analysis resulting in the increase of anodizing voltage causes the overpotential value and Tafel slope to show a steadily declining trend. This could highlight a potential strategy for customising electrocatalysts to increase efficiency.

ACKNOWLEDGEMENTS

The author would like to acknowledge the support from the Fundamental Research Grant Scheme (FRGS) under the grant number FRGS/1/2019/TK10/UNIMAP/02/2 from the Ministry of Higher Education Malaysia. Special thanks to Centre of Excellence for Frontier Materials Research (FrontMate) and Institute of Nano Electronic Engineering (INEE) for providing facilities and testing this project.

REFERENCES

- [1] Du, J., Xiang, D., Zhou, K., Wang, L., Yu, J., Xia, H., Zhao, L., Liu, H., & Zhou, W. (2022) Electrochemical hydrogen production coupled with oxygen evolution, organic synthesis, and waste reforming. *Nano Energy*. 104 (PA), 107875.
- [2] Amin, M., Shah, H. H., Fareed, A.G., Khan, W. U., Chung, E., Zia, A., Rahman Farooqi, Z. U., & Lee, C. (2022) Hydrogen production through renewable and non-renewable energy processes and their impact on climate change. *International Journal of Hydrogen Energy*.

- 47 (77), 33112–33134.
- [3] Yao, M., Sun, B., Wang, N., Hu, W., & Komarneni, S. (2019) Self-generated N-doped anodized stainless steel mesh for an efficient and stable overall water splitting electrocatalyst. *Applied Surface Science*. 480 (January), 655–664.
- [4] Gao, Y., Xiong, T., Li, Y., Huang, Y., Li, Y., & Balogun, M. S. J. T. (2019) A Simple and Scalable Approach to Remarkably Boost the Overall Water Splitting Activity of Stainless Steel Electrocatalysts. *ACS Omega*. 4 (14), 16130–16138.
- [5] Su, H., Jiang, J., Song, S., An, B., Li, N., Gao, Y., & Ge, L. (2023) Recent progress on design and applications of transition metal chalcogenide-associated electrocatalysts for the overall water splitting. *Chinese Journal of Catalysis*. 44 7–49.
- [6] Zhu, J., Hu, L., Zhao, P., Lee, L. Y. S., & Wong, K. Y. (2020) Recent Advances in Electrocatalytic Hydrogen Evolution Using Nanoparticles. *Chemical Reviews*. 120 (2), 851–918.
- [7] Anantharaj, S., Chatterjee, S., Swaathini, K. C., Amarnath, T. S., Subhashini, E., Pattanayak, D. K., & Kundu, S. (2018) Stainless Steel Scrubber: A Cost Efficient Catalytic Electrode for Full Water Splitting in Alkaline Medium. *ACS Sustainable Chemistry and Engineering*. 6 (2), 2498–2509.
- [8] Kim, M., Ha, J., Shin, N., Kim, Y. T., & Choi, J. (2020) Self-activated anodic nanoporous stainless steel electrocatalysts with high durability for the hydrogen evolution reaction. *Electrochimica Acta*. 364 137315.
- [9] Anantharaj, S., Ede, S.R., Karthick, K., Sam Sankar, S., Sangeetha, K., Karthik, P. E., & Kundu, S. (2018) Precision and correctness in the evaluation of electrocatalytic water splitting: Revisiting activity parameters with a critical assessment. *Energy and Environmental Science*. 11 (4), 744–771.
- [10] Lin, C. C., Hu, C. C., & Lee, T. C. (2009) Electropolishing of 304 stainless steel: Interactive effects of glycerol content, bath temperature, and current density on surface roughness and morphology. *Surface and Coatings Technology*. 204 (4), 448–454.
- [11] Jeong, C. (2022) A Study on Functional Hydrophobic Stainless Steel 316L Using Single-Step Anodization and a Self-Assembled Monolayer Coating to Improve Corrosion Resistance. *Coatings*. 12 (3), 395.
- [12] Lee, J., Choi, H. K., Kim, M. G., Lee, Y. S., & Lee, K. (2020) Formation of porous oxide layer on stainless steel by anodization in hot glycerol electrolyte. *Applied Chemistry for Engineering*. 31 (2), 215–219.