A New Accelerated Durability Test Protocol for Water Oxidation Electrocatalysts of Renewable Energy Powered Alkaline Water Electrolyzers

Ashraf ABDEL HALEEM, a, *, Kensaku NAGASAWA, a Yoshiyuki KURODA, a Yoshinori NISHIKI, b Awaludin ZAENAL, b and Shigenori MITSUSHIMA a

a Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
b De Nora Permelec, Ltd., 2023-15 Endo, Fujisawa 252-0816, Japan

* Corresponding author: hassan-ashraf-xj@ynu.ac.jp

© The Author(s) 2020. Published by ECSJ. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium provided the original work is properly cited. [DOI: 10.5796/electrochemistry.20-00156].

This is the final version of an authors' manuscript, submitted by the author(s) and accepted for publication after peer review and technical editing by the Editorial Board of The Electrochemical Society of Japan. This manuscript may contain minor errors or incomplete designs that do not affect the judgment for publication. It is the responsibility of the authors to correct any errors in the Just Accepted manuscript during galley proof review.
A New Accelerated Durability Test Protocol for Water Oxidation Electrocatalysts of Renewable Energy Powered Alkaline Water Electrolyzers

Ashraf Abdel Haleem\textsuperscript{a,*}, Kensaku Nagasawa\textsuperscript{a}, Yoshiyuki Kuroda\textsuperscript{a}, Yoshinori Nishiki\textsuperscript{b}, Awaludin Zaenal\textsuperscript{b}, Shigenori Mitsushima\textsuperscript{a}

\textsuperscript{a}Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama, 240-8501, Japan.

\textsuperscript{b}De Nora Permelec, Ltd., 2023-15 Endo Fujisawa 252-0816, Japan.

\textsuperscript{*}Corresponding author: hassan-ashraf-xj@ynu.ac.jp
Abstract

For electrocatalysts of oxygen evolution reaction (OER), a new accelerated durability test (ADT) protocol is presented. The protocol is designed to closely mimic the fluctuations of renewable energies. The unit cycle of the current ADT protocol represents the “ON / OFF” operation mode. In the “ON” step, the electrolyzer operates under a DC current of 0.6 A cm\(^{-2}\). In the “OFF” step, the electrocatalyst is subjected to a constant potential that is clearly more cathodic than its OER onset potential (namely, 0.3, 0.5, and 0.7 V vs. RHE) for 10 or 60 s. The transition from the “ON” state to the “OFF” state occurs through a cathodic linear sweep voltammetry of a fast sweep rate to mimic the sudden changes in the renewable power. A NiCoO\(_x\)/Ni-mesh electrode was used as a case study. The electrode showed remarkable durability under continuous operation (\(i = 0.6\) A cm\(^{-2}\)) for about 900 hours. However, it did suffer severe degradation after a certain number of ADT cycles, and the rate of degradation mainly depends on the potential value and the duration of the “OFF” step. Interestingly, the inclusion of the 10-sec open-circuit potential step after the “ON” step clearly mitigates the impact of energy fluctuations on the durability of OER electrocatalysts.

Key words: Alkaline water electrolysis; water oxidation catalyst; accelerated durability test.
1. Introduction

The power-to-gas concept is widely accepted as a prominent approach to stabilizing electricity grids with a high level of renewable energy penetration.\textsuperscript{1–3} In recent years, hydrogen received great attentions as an energy carrier (storage) because it is clean fuel with a relatively high energy density and works with fuel cells.\textsuperscript{4–7} Nowadays, the main share of global hydrogen is produced from fossil fuels, which are neither clean nor sustainable.\textsuperscript{8} On the other hand, the widely popular vision of the hydrogen economy, which relies on hydrogen as the main fuel, can become a reality if hydrogen can be produced from domestic environmentally friendly energy sources.\textsuperscript{9,10} One of the most promising approaches is the coupling of renewable energy generators, particularly solar panels, with water electrolyzers.\textsuperscript{10–12}

So far, there are three types of water electrolysis technology: alkaline water electrolysis, proton exchange membrane water electrolysis, and solid oxide water electrolysis.\textsuperscript{13,14} Of the three technologies available, alkaline water electrolysis (AWE) is the most technologically mature.\textsuperscript{15} The additional merits of AWE include simple design, relatively low cost, long service life, high system-level reliability.\textsuperscript{16} Owing to the sluggish kinetics of OER and the extremely harsh environment in which the OER takes place, durability of OER electrocatalysts is a major issue.\textsuperscript{17} Moreover, the fluctuant and intermittent nature of the renewable energy sources add further stressors on the OER electrodes and thus accelerates their degradation. The metal-oxide material of the electrocatalyst is in a high oxidation state during the operation of the electrolyzer and it is subjected to unfavorable electrochemical reduction during the electrolyzer shutdown. In industrial AWE systems, after switching off
the bipolar plate electrolyzer, the cathode and anode on both sides of any bipolar plate are electrically connected through the structure of the bipolar plate and are ionically connected through the electrolyte in the manifolds. This induces a reverse current to flow through this closed circuit between the negatively charged cathode and the positively charged anode on either side of the bipolar plate.\textsuperscript{18,19} Therefore, the cathode material is oxidized, and the anode material is reduced during the stopping time.

Evaluating the durability of the OER electrodes throughout their entire service life under actual conditions is not practical, as the target service life of the electrolyzer is five to ten years. Therefore, accelerated durability tests (ADT) that simulate the actual conditions and stimulate the degradation mechanisms in a shorter timescale are of great importance for the development of robust OER electrocatalysts. To our knowledge, reports presenting accelerated durability testing protocols for OER electrocatalysts in alkaline water electrolysis are limited. They mainly introduced ADT protocols based on cyclic voltammetry or cyclic galvanometry for several consecutive cycles to assess the durability of OER electrocatalysts in AWE systems.\textsuperscript{20–25} In fact, these ADT protocols did not mimic the actual operation of the AWE electrolyzers in the industry, particularly under intermittent renewable power sources.\textsuperscript{22} In other studies, the impact of the fluctuating current (sinusoidal, triangular, and square waveforms) and voltage (sinusoidal) sources on the water splitting efficiency (H\textsubscript{2} yield) were investigated, however the durability issue was not discussed.\textsuperscript{26,27}

In the development of polymer electrolyte fuel cell systems, ADT test protocols are proposed as standard potential step cycles for load fluctuation and standard potential sweep cycles for start and stop operation of vehicles for a free-volume electrochemical cell and a
laboratory scale fuel cell recommended by the Fuel Cell Commercialization Conference of Japan (FCCJ) and the United States Department of Energy (DOE). These protocols are shared in industry and have contributed to new material developments. The protocols for fuel cells are potential or cell voltage control methods.\textsuperscript{28-30}

In this study, a new ADT protocol was developed to assess the robustness of the OER electrode in AWE under the dynamic operating mode. In order to simulate the fluctuations and intermittent nature of renewable energies, the current ADT protocol combines current and potential control steps to simulate the "ON/OFF" operating mode of the electrolyzer. Most likely, this protocol will be widely accepted as a standard ADT and thus contribute to the development of robust OER electrocatalysts for the emerging renewable hydrogen industry. It is noteworthy that, prior to ADT experiments, the current electrocatalyst was subjected to a specific electrochemical pre-treatment process in order to improve its OER activity.

2. Experimental

2.1 Preparation of the OER electrocatalyst electrode

The thermal decomposition method was used to prepare the standard Nickel-Cobalt spinel anode as follows:

- A blasted mesh (6.0 mm as LW, 3.7 mm as SW, and 0.8 mm as thickness) made of nickel was etched in boiling 20 % hydrochloric acid and rinsed with pure water.

- The coating precursor of the standard anode was a highly concentrated aqueous solution of Ni and Co salts in a 1:1 molar ratio.
- The Ni-mesh was coated with the precursor, dried, and then thermally decomposed at more than 500 °C for several minutes.
- The coating, drying, and decomposition processes were repeated several times to prepare the spinel oxide film with a suitable thickness of several microns.

The geometrical surface area of the working electrode was 1.0 cm².

2.2 The electrochemical measurements

All the electrochemical experiments were conducted using a three-electrode (500 ml) electrochemical cell made of polytetrafluoroethylene (PTFE). The NiCoOₓ (the OER electrocatalyst) on Ni-mesh was used as the working electrode (anode), the reversible hydrogen electrode (RHE) was used as the reference electrode, and a spiral nickel wire was used as the counter electrode (cathode).

The working electrode (NiCoOₓ/Ni-mesh) was connected vertically in the 3-electrode cell by a Ni wire that shielded by a heat shrink plastic tube. The distance between the working electrode and the Luggin capillary of the reference electrode was maintained within ~1.0 cm. The nickel wire (cathode) was chemically etched in a boiling dilute aqueous hydrochloric acid solution for approximately 5 min. The cathode was surrounded by a cylindrical tube made of the Zirfon membrane, which was likely to prevent the electrochemically generated hydrogen from spreading into the electrolyte of the cell. The electrolyte used in this study was an aqueous KOH solution of 7.0 molar (7.0 M), which was prepared by dissolving a specific amount of KOH (Junsei Chemical Co., Ltd) in deionized water (milli-Q quality water, 18 MΩ cm). The KOH solution of the 3-electrode cell and the reference electrode was saturated with nitrogen and hydrogen, respectively, by bubbles for 20
min prior to each experiment and continued over time of the experiment. The electrolyte
temperature was maintained at 80 and 25 °C during the pre-treatment (electrochemical
activation) and the durability test experiments, respectively. The electrochemical experiments
were performed using a Bio-Logic SAS potentiostat (model: VSP-300) which is controlled by
a specialized software (EC-Lab V11.30).

The cyclic voltammetry (CV) measurements were performed in a specific potential
window (0.5 to 2.0 V vs. RHE) at different scan rates, namely 5, 50, and 150 mV s⁻¹ for 3
consecutive cycles.

The electrochemical impedance spectroscopic (EIS) measurements were performed
under potentiostatic conditions (PEIS) of potential values equal to 1.5, 1.6, and 1.7 V vs.
RHE. An alternating electric current of the frequency range of 1.0 MHz-100 mHz with
amplitude of 10 mV was used in this experiment. EIS measurements were performed using
the same potentiostat mentioned hereinabove. The ohmic resistance, the electrolyte resistance
between the anode and the reference electrode, obtained in the high-frequency EIS
measurement was used to compensate for the \(iR\) drop and thus to obtain \(iR\)-free potential
values.

2.3 Electrochemical pre-treatment of the electrocatalyst electrode

Prior to the ADT experiments, the as-prepared samples were electrochemically treated to
improve their OER activity. The pre-treatment (aging or conditioning) procedure was
accomplished by performing water electrolysis under the application of a DC current of 1.0 A
cm⁻² for 2 h at temperature of 80 °C. Various electrochemical characterizations of the anode
were carried out to explore the effectiveness of the pre-treatment condition.
2.4 Accelerated degradation test (ADT) protocol

The ADT protocol was primarily designed to examine the durability of the electrode against the repeated fluctuations of the renewable power sources. The protocol comprises the steady state operation of the alkaline water electrolyzer under a DC current of 0.6 A cm\(^{-2}\) in addition to other potential control steps most likely to mimic fluctuations of the renewable energy sources. Figure 1 shows a unit cycle of the current ADT protocol. The ADT cycle begins with the normal operation mode under chronopotentiometry condition (CP-step) of 0.6 A cm\(^{-2}\) for 1 min. Afterward the power fluctuation was implemented as a cathodic linear sweep voltammetry (LSV-step) with a fast sweep rate (v) followed by a chronoamperometry step (CA-step) of a certain potential value (\(E_{\text{min}}\)). The value of \(E_{\text{min}}\) is much less than the open circuit potential (OCP) of the anode immediately after termination of electrolysis, which is equal to about 1.5 V vs. RHE, for a specified period (\(t_{\text{min}}\)). In fact, \(E_{\text{min}}\) represents the anode potential while the reverse current flows in the bipolar plate electrolyzer for industrial AWE systems. In addition, the effect of inserting a 10-second open circuit potential step between the CP-step and the LSV-step of the ADT unit cycle has been studied, the schematic diagram of the modified ADT is shown in Fig. S1. After each group of 200 ADT cycles, the cyclic voltammetry (CV) and the EIS measurements were performed to figure out the state of the catalytic activity of the electrode at that stage of the ADT experiment. Ultimately, the ADT lasted for 2000 cycles (10 groups of 200 cycles each). The total time of the ADT experiment, including the 2000 ADT cycles and the needed electrochemical measurements, is about 70 h.

3. Results and Discussion

3.1 Electrochemical pre-treatment of the electrode
Figure 2 (a) illustrates the anode potential during the pre-treatment experiment. The figure shows a marked gradual decrease in the anode potential over time, especially in the early stage of the experiment. After about 1.5 h of the ageing experiment the electrode reaches a steady-state condition with a negligible potential decrease. Figure 2 (b) shows the polarization curves of the anode before and after the conditioning experiment. The figure reveals a pronounced cathodic shift for the onset potential of the water oxidation reaction in case of the electrochemical pre-treated electrode. In addition, the Tafel slope of the electrode decreased from 84 mV dec⁻¹ to 75 mV dec⁻¹ after the pre-treatment experiment, as shown in Fig. S2 (a). The redox peaks have been clearly increased due to the application of the present electrochemical conditioning procedure, as shown in the inset of Fig. 2 (b). This denotes the growth of the Ni-based hydroxide / oxy-hydroxide layer at the electrode surface. This observation could explain the improved OER activity of the anode after the electrochemical aging experiment. Furthermore, the electrochemical impedance (EIS) of the anode half-cell was measured before and after the pre-treatment experiment and the resulting Nyquist plots are shown in Fig. S2 (b) and the equivalent circuit is shown in Fig. S3. Table S1 presents the parameters of the electrochemical impedance before and after the pre-treatment. There is a clear decrease in the electrolyte resistance ($R_1$) and electrode-related resistance ($R_2$) from 285 and 31 to 255 and 25 mΩ cm², respectively. This indicates the increase of the electrode electrical conductivity after the electrochemical aging procedure. In addition, there is a noticeable decrease in the charge transfer resistance ($R_3$) from 100 to 80 mΩ cm² and a clear increase in the double-layer capacitance ($C_3$) from 64 to 79 mF cm⁻². This observation indicates that the electrochemically active sites at the electrode surface have been increased.
due to the electrode conditioning process. Accordingly, these results emphasize the effectiveness of the pre-treatment condition towards improving the water oxidation catalytic activity of the present electrode.

3.2 The influence of the potential value of CA-step ($E_{\text{min}}$)

The electrode durability test was carried out at three different $E_{\text{min}}$ values, namely 0.3, 0.5, and 0.7 V vs. RHE, while the duration of this step ($t_{\text{min}}$) was maintained at 1 min. Figure 3 shows electrode potential values, corresponding to current density of 100 mA cm$^{-2}$, versus ADT cycles. These potential values were taken from the anodic scans of the polarization curves shown in Figs. S4 (a) and (b). Figure 3 reveals that the electrode behavior under $E_{\text{min}}$ equal to 0.3 and 0.5 V are almost identical, however the electrode shows better stability against fluctuations with $E_{\text{min}} = 0.7$ V. In addition, EIS measurements for the anode half-cell show a significant increase in the electrochemical impedance in the case of $E_{\text{min}} = 0.5$ V compared to $E_{\text{min}} = 0.7$ V after 800 ADT cycles, as shown in Fig. S5. This means that the more positive the value of $E_{\text{min}}$, the less the stress on the anode. Essentially, the current electrode behavior under this ADT protocol can be divided into three major regions based on the anode potential pattern associated with the CP-steps, as shown in Fig. S6. Region A, in which the electrode shows a relatively stable performance. Region B, during which a fast degradation of the electrode takes place. In region C the electrode loses its OER activity completely except for the low activity of the metallic substrate.

3.3 The influence of the CA-step duration ($t_{\text{min}}$)

The impact of the value of $t_{\text{min}}$ on the durability of the electrode was studied at $E_{\text{min}}$ equal to 0.5 V vs. RHE and $t_{\text{min}}$ equal to 10 and 60 s. Figure 4 shows the anode potential
corresponding to 100 mA cm\(^{-2}\) versus the ADT cycles for the two \(t_{\text{min}}\) values based on the cyclic voltammetry measurements shown in Figs. S4 (a) and S7. Figure 4 reveals the significant effect of \(t_{\text{min}}\) on the durability of the electrode. The electrode shows much better durability under ADT of which \(t_{\text{min}} = 10\) s compared to \(t_{\text{min}} = 60\) s. The EIS measurements shown in Fig. S8 emphasize the impact of \(t_{\text{min}}\) on the electrode performance. After 800 cycles of ADT, the electrochemical impedance of the sample tested at \(t_{\text{min}} = 60\) s was significantly increased compared to that of \(t_{\text{min}} = 10\) s. In addition, the electrode tested at \(t_{\text{min}} = 10\) s shows a stable OER activity for a much greater number of ADT cycles (region A becomes much wider) as shown in Fig. S9. This could be due to the electrochemical reduction reaction that takes place at the anode surface when its potential goes more cathodic than its open circuit potential after the termination of the water electrolysis reaction.\(^{18,23,19}\) Therefore, when the duration of the stopping potential (\(t_{\text{min}}\)) was reduced from 60 s to 10 s the effect of electrochemical reduction reaction on the oxidized species at the electrode surface was minimized and thus the electrode showed better stability against the dynamic operation mode. This means that the value of the stopping potential (\(E_{\text{min}}\)) as well as its duration (\(t_{\text{min}}\)) determine the level of stresses on the anode. In addition, the recurring transition between reducing and oxidizing conditions triggers the electrocatalyst dissolution and/or detachment.\(^{35,36}\) The photographic images (by the CCD camera) of the fresh and ADT tested sample shown in Fig. S10 reveal complete detachment and/or dissolution of the active layer after ADT.

3.4 The influence of the sweep rate (\(v\)) of LSV-step

Basically, in the current ADT protocol, the transition from the CP-step (water electrolysis
at 0.6 A cm$^{-2}$) to the CA-step (stopping of the water electrolysis at anode potential of $E_{\text{min}}$) occurs at a high sweep rate ($v = 500 \text{ mV s}^{-1}$). The cathodic LSV with a high sweep rate closely resembles the actual fluctuations of the renewable power sources. However, a linear sweep voltammetry with a much lower sweep rate ($v = 50 \text{ mV s}^{-1}$) was studied for comparison. Figure 5 shows the anode potential at 100 mA cm$^{-2}$ versus ADT cycles of two samples tested under $v$ equal to 50 and 500 mV s$^{-1}$. The figure reveals that the electrode shows better durability under the high sweeping rate. In the 600–1000 ADT cycles range, the electrode potential values of $v = 50 \text{ mV s}^{-1}$ are slightly higher than that of $v = 500 \text{ mV s}^{-1}$. In addition, the impact of the cathodic scan rate on electrode durability becomes more pronounced at the higher current density (0.6 A cm$^{-2}$), as shown in Fig. S11. The figure emphasizes the negative effect of the slow scan rate on the durability of the electrode. The stable region (region A) becomes narrower in the case of $v = 50 \text{ mV s}^{-1}$. It is worthy to note that the LSV interval of $v = 50 \text{ mV s}^{-1}$ is 10 times greater than that of $v = 500 \text{ mV s}^{-1}$. This may indicate that the anode was under a certain stress during the duration of cathodic scan of the ADT test.

3.5 The influence of inserting OCP-step immediately after the CP-step

The impact of inserting an open circuit potential step (OCP-step) of interval equals 10 s between the CP-step and the cathodic LSV step of the ADT protocol on the durability of the electrode was studied at $E_{\text{min}} = 0.5 \text{ V vs. RHE}$, $t_{\text{min}} = 60 \text{ s}$, and $v = 500 \text{ mV s}^{-1}$. Figure 6 illustrates the anode potential corresponding to 100 mA cm$^{-2}$ versus the ADT cycles. These potential values were derived from the CV measurements (shown in Figs. S4 (a) and S12) for two samples tested with and without the embedding of the OCP-step. Although the interval of
the OCP-step is relatively small (10 s), it does have a significant impact toward improving the durability of the current electrode against fluctuations in the power source. Figure S13 shows the anode potential associated with water electrolysis at 0.6 A cm$^{-2}$ versus the ADT cycles of two electrodes tested with and without the inclusion of the OCP-step. The figure emphasizes the significance of the OCP-step; the range of the ADT cycles under which the anode exhibits stable water oxidation performance (region A) was clearly extended and the rate of degradation during the subsequent region (region B: fast degradation zone) was noticeably decreased owing to the presence of OCP-step. Additionally, the electrochemical impedance of the anode half-cell after 800 cycles of ADT with OCP-step is much smaller than that without the OCP-step, as shown in Fig. S14. It is noteworthy that in the last stage of the ADT experiment (above 1600 cycles) the anode potential in case of OCP-step is clearly lower than that without OCP-step. This could imply that the OCP-step mitigated the corrosion of the Ni-substrate that has a certain activity toward OER. To the best of our knowledge, this positive effect of OCP-step on the durability of OER electrocatalysts under dynamic conditions is completely new observation. It can be concluded that direct frequent transitions between reduction and oxidation conditions stimulate electrocatalyst dissolution and/or detachment from the substrate. However, when an OCP step (break) is included between the reduction and the oxidation steps of the ADT, the durability of the electrocatalyst is greatly improved. The mechanism behind this phenomenon is not yet fully understood. It seems that a relaxation in the electrocatalyst structure may take place during the open circuit step before the electrocatalyst undergoes a new reduction cycle. The influence of the OCP-step is very promising as it can be easily implemented in the industry by connecting a relatively
small-capacity backup battery in parallel with the electrolyzer. The proposed system modification can remarkably improve the durability of the anode against fluctuations in the renewable power source.

3.6 The stability of the electrode under the steady state operation

Although the aim of this study is to provide an effective ADT protocol for the anode of the alkaline water electrolyzer under fluctuating power sources, it is essential to examine the same electrode under the steady-state water electrolysis condition to underline its worth and to highlight the impact of fluctuations of the power source on the durability of OER electrocatalysts. In this experiment, the KOH electrolyte was basically renewed approximately every 150 h. However, in the late stage of the experiment (the last 300 h) we just injected deionized water into the cell to compensate for the evaporated and the dissociated water amount. Figure 7 shows the anode potential associated with water electrolysis under a DC current of 0.6 A cm\(^{-2}\) for 900 h. The electrode showed a very stable performance for water oxidation under the steady-state electrolysis condition. In addition, the OER activity of the electrode improved during the experiment, especially in the early stage of the experiment, as observed in the Nyquist plots of the electrochemical impedance measurements at different periods of the test, as shown in Fig. S15. The photographic image of the tested sample, in contrast to the samples tested under the ADT protocol, did not show any sign of active layer detachment as shown in Fig. S16. This experiment implies the robustness of the current OER electrocatalyst under steady state operation. However, further improvement is still necessary to improve its durability under the harsh dynamic condition.

4. Conclusions
To develop OER electrocatalysts for alkaline water electrolyzers powered by renewable energy sources, a new accelerated durability test protocol has been developed. The unit cycle of the present ADT protocol consists of a current control step and a potential control step; the former simulates the steady-state operation and the latter mimics the expected fluctuations of the renewable power sources. The NiCoOₓ/Ni-mesh electrode was used as a case study. The electrode showed a remarkable robustness under steady-state operation of \( i = 0.6 \text{ A cm}^{-2} \) for 900 h. However, it experienced a rapid deterioration in the OER performance after a certain number of ADT cycles. The degradation rate depends mainly on the potential value \( (E_{\text{min}}) \) and the duration \( (t_{\text{min}}) \) of the potential control step. \( E_{\text{min}} \) represents the anode potential while the reverse current flows in the bipolar plate electrolyzer in the industrial AWE systems. This means that after turning off the electrolyzer, the anode undergoes an undesirable electrochemical reducing reaction. The electrocatalyst degradation during the ADT is associated with film detachment from the substrate. Moreover, the inclusion of the open circuit step just after the termination of the water electrolysis step enhances significantly the durability of the OER electrocatalyst under such harsh dynamic condition. It is worthy to mention that, the pre-treatment procedure which was water electrolysis at 80 °C under the application of 1.0 A cm⁻² for 2 h effectively improved the catalytic activity of the OER electrocatalyst.

**Acknowledgments**

This study was based on results obtained from P14021 of the development of Fundamental Technology for Advancement of Water Electrolysis Hydrogen Production in Advancement of
Hydrogen Technologies and Utilization Project commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

**ORCID**

Ashraf Abdel Haleem: 0000-0002-9656-6724

Shigenori. Mitsushima: 0000-0001-9955-2507

**Supporting Information:** The Supporting Information is available on the website at DOI: xxxxxxx.
References

1. A. Maroufmashat and M. Fowler, *Energies*, **10**, 1089 (2017).

2. J. Ma, Q. Li, M. Kühn, and N. Nakaten, *Renew. Sustain. Energy Rev.*, **97**, 478 (2018).

3. B. Lyseng, T. Niet, J. English, V. Keller, K. Palmer-Wilson, B. Robertson, A. Rowe, and P. Wild, *Int. J. Hydrogen Energy*, **43**, 1966 (2018).

4. A. Midilli, M. Ay, I. Dincer, and M. A. Rosen, *Renew. Sustain. Energy Rev.*, **9**, 255 (2005).

5. L. Z. Ouyang, J. M. Huang, H. Wanga, Y. J. Wena, Q.A. Zhang, D.L. Sun, and M. Zhu, *Int. J. Hydrogen Energy*, **38**, 2973 (2013).

6. A. M. Abdalla, S. Hossain, O. B. Nisfindy, A. T. Azad, M. Dawood, and A. K. Azad, *Energy Convers. Manag.*, **165**, 602 (2018).

7. P. P. Edwards, V. L. Kuznetsov, W. I. F. David, and N. P. Brandon, *Energy Policy*, **36**, 4356 (2008).

8. P. Nikolaidis and A. Poullikkas, *Renew. Sustain. Energy Rev.*, **67**, 597 (2017).

9. R. H. Lin, Y. Y. Zhao, and B. D. Wu, *Int. J. Hydrogen Energy*, **45**, 20164 (2020).

10. J. Turner, G. Sverdrup, M. K. Mann, B. K. Pin-Ching Maness, and R. J. E. and D. B. Maria Ghirardi, *Int. J. Energy Res.*, **32**, 379 (2008).

11. A. Mohammadi and M. Mehrpooya, *Energy*, **158**, 632 (2018).

12. J. Chi and H. Yu, *Chinese J. Catal.*, **39**, 390 (2018).

13. M. A. Khan, H. Zhao1, W. Zou1, Z. Chen1, W. Cao1, J. Fang, J. Xu, L. Zhang, and J. Zhang, *Electrochem. Energy Rev.*, **1**, 483 (2018).

14. M. David, C. Ocampo-Martínez, and R. Sánchez-Peña, *J. Energy Storage*, **23**, 392 (2019).

15. J. Brauns and T. Turek, *Processes*, **8**, 248 (2020).

16. N. V. Kuleshov, V. N. Kuleshov, S. A. Dovbysh, S. A. Grigoriev, S. V. Kurochkin, and P. Millet, *Int. J. Hydrogen Energy*
Energy, 44, 29441 (2019).

17. E. Fabbri and T. J. Schmidt, ACS Catal., 8, 9765 (2018).

18. Y. Uchino, T. Kobayashi, S. Hasegawa, I. Nagashima, Y. Sunada, A. Manabe, Y. Nishiki, and S. Mitsushima,
   Electrocatalysis, 9, 67 (2018).

19. Y. Uchino, T. Kobayashi, S. Hasegawa, I. Nagashima, Y. Sunada, A. Manabe, Y. Nishiki, and S. Mitsushima,
   Electrochemistry, 86, 138 (2018).

20. D. Delgado, F. Bizzotto, A. Zana, and M. Arenz, ChemPhysChem, 20, 3147 (2019).

21. S. Fujita, I. Nagashima, Y. Sunada, Y. Nishiki, and S. Mitsushima, Electrocatalysis, 8, 422 (2017).

22. Y. Kuroda, T. Nishimoto, and S. Mitsushima, Electrochim. Acta, 323, 134812 (2019).

23. S. Fujita, I. Nagashima, Y. Nishiki, C. Canaff, T. W. Napporn, and S. Mitsushima, Electrocatalysis, 9, 162 (2018).

24. A. Maljusch, O. Conradi, S. Hoch, M. Blug, and W. Schuhmann, Anal. Chem., 88, 7597 (2016).

25. F. Davodi, E. Muhlhausen, M. Tavakkoli, J. Sainio, H. Jiang, B. Gokce, G. Marzun, and T. Kallio, ACS Appl. Mater.
   Interfaces, 10, 31300 (2018).

26. Z. Dobó and Á. B. Palotás, Int. J. Hydrogen Energy, 42, 5649 (2017).

27. Z. Dobó and Á. B. Palotás, Int. J. Hydrogen Energy, 41, 11849 (2016).

28. http://fccj.jp/pdf/23_01_kt.pdf.

29. H. Yano, I. Arima, M. Watanabe, A. Iiyama, and H. Uchida, J. Electrochem. Soc., 164, F966 (2017).

30. United States Department of Energy, Fuel Cells, 2 (2007).

http://www1.eere.energy.gov/hydrogenandfuelcells/fuelcells/pdfs/component_durability_profile.pdf.

31. M. E. G. Lyons, R. L. Doyle, J. Godwin, M. O’Brien, and L. Russell, J. Electrochem. Soc., 159, H932 (2012).

32. M. Alsabet, M. Grdeń, and G. Jerkiewicz, Electrocatalysis, 6, 60 (2014).

33. A. K. Taylor, I. Andreu, and B. D. Gates, ACS Appl. Energy Mater., 1, 1771 (2018).

34. E. López-Fernández, J. Gil-Rostra, J. P. Espinós, A. R. González-Elpe, A. de Lucas Consuegra, and F. Yubero, ACS
Catal., 10, 6159 (2020).

35. M. Bernt, A. Hartig-Weiβ, M. F. Tovini, H. A. El-Sayed, C. Schramm, J. Schroter, C. Gebauer, and H. A. Gasteiger, Chem. Ing. Tech., 92, 31 (2020).

36. A. Weiß, A. Siebel, M. Bernt, T. H. Shen, V. Tileli, and H. A. Gasteiger, J. Electrochem. Soc., 166, F487 (2019).
Figure captions:

1- Fig. 1. Schematic diagram of a unit cycle of the accelerated durability test protocol.

2- Fig. 2. (a) The anode-electrode potential under the application of 1.0 A cm⁻² for 2 h at temperature of 80 °C in KOH (7 M) solution as a pre-treatment (activation) procedure, (b) the polarization curves of the anode before (red) and after (black) the activation.

3- Fig. 3. The anode potentials corresponding to current density of 0.1 A cm⁻² versus the ADT cycles of samples tested at $E_{\text{min}}$ equals 0.3, 0.5, and 0.7 V vs RHE.

4- Fig. 4. The anode potentials corresponding to current density of 0.1 A cm⁻² versus the ADT cycles of samples tested at $E_{\text{min}} = 0.5$ V vs RHE of duration ($t_{\text{min}}$) equal to 10 s and 60 s.

5- Fig. 5. The anode potentials corresponding to current density of 0.1 A cm⁻² versus the ADT cycles of samples tested at $E_{\text{min}} = 0.5$ V, $t_{\text{min}} = 60$ s, and LSV with $\nu = 50$ and 500 mV s⁻¹.

6- Fig. 6. The anode potentials corresponding to current density of 0.1 A cm⁻² versus the ADT cycles of samples tested at $E_{\text{min}} = 0.5$ V, $t_{\text{min}} = 60$ s, LSV of $\nu = 500$ mV s⁻¹, with and without the inclusion of OCP ($t_{\text{OCP}} = 10$ s) after the CP-step.

7- Fig. 7. The anode potential corresponding to water electrolysis under a steady-state condition of $i = 0.6$ A cm⁻² for about 900 h.
Figure: 1

ADT unit cycle

- \( i_{\text{CD}} = 600 \text{ mA/cm}^2 \), 60 s
- LSV: 850 or 900 mV/s
- \( E_{\text{init}} = 0.3, 0.5, \text{ or } 0.7 \text{ V} \)
- \( t_{\text{pulse}} = 10 \text{ or } 60 \text{ s} \)
Figure 2:
Figure 3:
Figure 4:
Figure 5:
Figure 6:
Figure 7: