

Potential Regulation for Stable Electrocatalysts in Alkaline Water Electrolyzers during Dynamic On and Off Operation through Double-Layer Capacitance Engineering

Published as part of *The Journal of Physical Chemistry C* special issue "Degradation of Electrochemical Materials in Energy Conversion and Storage".

Tengisbold Gankhuyag, Keisuke Obata, and Kazuhiro Takanabe*



Cite This: *J. Phys. Chem. C* 2025, 129, 18043–18050



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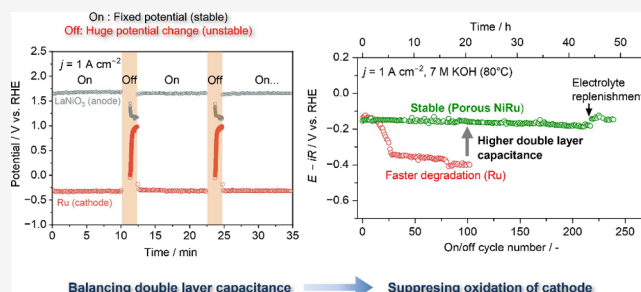


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ABSTRACT: This study explores the impact of reverse current on catalyst degradation in alkaline water electrolysis (AWE) systems that are powered by renewable energy sources (RESs). AWE is a promising technology for green hydrogen generation, but frequent on/off cycling due to RES intermittency poses challenges, including catalyst degradation. This research focuses on two key electrocatalysts: Ru for the hydrogen evolution reaction and LaNiO₃ for the oxygen evolution reaction. The stability of the catalysts was investigated under dynamic operating conditions. The experiments reveal that the redox capacitance is discharged under closed-circuit conditions, which generates a substantial shift of the applied potential in the reverse direction in both the cathode and anode. As a result, reverse current flows and affects the catalyst stability. The Ru cathode degradation was studied with anodes of varying double-layer capacitance (C_{dl}). Porous NiRu cathodes with higher C_{dl} values showed better balance with LaNiO₃ anode, which reduced the changes in the resultant reaching electrode potential and thus mitigated degradation due to dissolution of Ru species. This study provides valuable insights for the design of stable electrode materials for AWE systems that operate under fluctuating conditions and emphasizes the importance of tuning the anode–cathode capacitance ratios to enhance durability and efficiency.



INTRODUCTION

Hydrogen is widely recognized as a key energy carrier for a future carbon-neutral society due to its high calorific value, zero carbon production, and versatile applications, such as the transportation sector, chemical industry, and heat and power generation for households and industry.^{1,2} Green hydrogen generation via water electrolysis using renewable energy sources (RESs) is particularly promising due to its zero carbon footprint.³ Alkaline water electrolysis (AWE) is the most mature water electrolysis technology and offers the advantage of using non-noble materials such as nickel and iron as catalysts, which contributes to its lower cost.^{4,5} AWE has demonstrated potential to achieve good electrochemical performance (2 A cm⁻² at cell voltage <2 V) by minimizing Ohmic losses through efficient bubble evacuation and use of high-activity catalysts.^{6–8}

Extensive research has focused on enhancing the current density, but the stability of the RES-powered AWE is still an issue. A significant challenge is catalyst degradation due to frequent on/off (startup/shutdown) cycling of the electrolyzer, which is impeding the widespread use of RES-powered AWE. This cyclic operation is necessary for safety, as the electrolyzer

system must be shut down to prevent explosion if the H₂ concentration in O₂ reaches 2 vol %.^{9–11} When using porous diaphragms such as commercial Zirfon, hydrogen impurities in the oxygen increase during low-current-density operation, which limits the reduced operation under partial load of the electrolyzer to 25–40% of its full load.^{12–14}

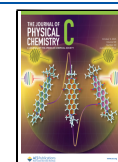
In a typical industrial AWE electrolyzer stack, multiple cells are connected in series through a metallic bipolar plate, and the cathode and anode are polarized due to external electromotive force during electrolysis (Figure 1a). In this bipolar configuration, the cathode and anode of adjacent cells are connected electrically through the bipolar plate as well as ionically through the electrolyte manifold and diaphragms at the same time, making a closed circuit. Thus, A spontaneous

Received: July 6, 2025

Revised: September 12, 2025

Accepted: September 16, 2025

Published: September 25, 2025



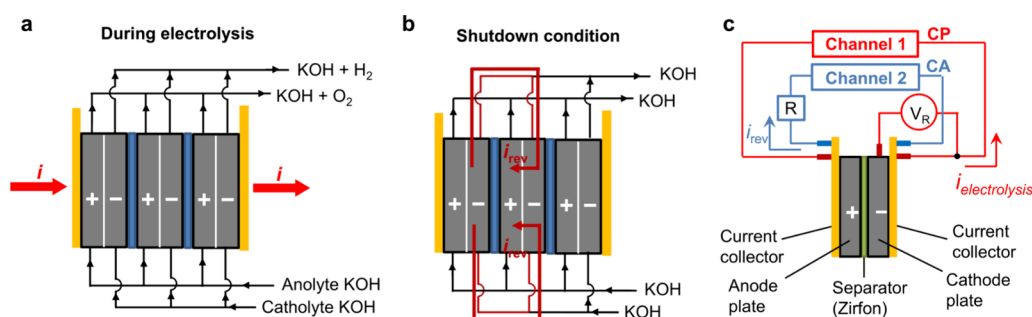


Figure 1. (a) Industrial AWE stack during electrolysis. (b) Flow of reverse current upon shutdown in an industrial AWE stack. (c) Experimental single-cell setup that mimics a cell stack, which was used to perform electrolysis ($i_{\text{electrolysis}}$) and measure the reverse current (i_{rev}).

self-discharge process is initiated upon shutdown to close the potential difference between the anode and cathode, which generates a reverse current. Reverse current with the opposite direction to that of the electrolysis current flows through the closed circuit until the anode and cathode reach the same rest potential (Figure 1b). The reverse current induces an unfavorable reduction of the anode catalyst and oxidation of the cathode catalyst, which accelerates their degradation. Therefore, it is necessary to consider this on/off cycling effect on catalyst degradation in long-term stability evaluations under potentiostatic or galvanostatic conditions.^{15,16}

Haleem et al. studied the effect of operating parameters such as the current density, temperature, and electrolyte flow rate on the reverse current in a four-cell stack configuration. Their experiment showed that rapid cooling of the cell and stopping the electrolyte flow immediately after shutdown can reduce the overall reverse current. Furthermore, if the anode has a larger charge capacity than the cathode on the same bipolar plate, the cathode is subject to more stress, which makes it more susceptible to corrosion.¹⁷ Oda et al. investigated the discharge behavior of metal oxide-based electrocatalysts and found that the discharge capacity of an electrocatalyst, which should reflect the amount of reverse current during shutdown, is proportional to its Brunauer–Emmett–Teller (BET) surface area.¹⁸

Nickel mesh electrodes were employed in a two-cell stack, and the nickel mesh on the cathode side was oxidized, while that of the anode side was reduced during reverse current. The major redox couple during the reverse current was assigned to $\text{NiO}_2/\text{NiOOH}$.¹⁹ The most important insight from these studies is that the anode and cathode materials should be chosen based not only on their activities but also on their charge capacities in order to minimize the degradation resulting from reverse current.

A recent study by Wang et al. showed that the nickel cathode is prone to severe degradation due to irreversible oxidation of nickel to β -nickel hydroxide during shutdown conditions.²⁰ Kim et al. also found that the Ni cathode is unstable and demonstrated that a Pb coating is effective for preventing the degradation of Ni cathodes under repeated shutdown conditions.^{21,22} Although the Pb/Ni electrocatalyst was tolerant of reverse current, Pb is highly toxic to the environment, including humans, animals, and plants.²³ Kim et al. suggest that the impact of anode reduction during reverse current is negligible, but other studies clearly show that oxygen evolution reaction (OER) catalysts are also prone to reverse current and deactivate faster under such conditions than in constant operation conditions. For example, in nickel cobalt-

based OER catalysts, severe deactivation occurs due to detachment of the catalyst from the nickel substrate when reverse current occurs.^{24–26}

Many studies employed an accelerated degradation test (ADT), in which the electrocatalyst was subjected to a constant rest potential that is more cathodic than its OER onset potential, which simulated frequent on/off cycles in the AWE powered by intermittent renewable energy. ADTs in a three-electrode system can help to evaluate the durability of electrocatalysts reasonably with much simpler experimental setups. Nevertheless, the combination of the anode and cathode is crucial for stability, so long-term durability tests using an actual complete AWE cell give more valuable insights into catalyst degradation from the perspective of industrial applications. For example, Sha et al. demonstrated intermittent alkaline seawater electrolysis in a complete AWE cell using a NiCoP-based cathode, which demonstrated that phosphate ion formation and a cobalt oxide passivation layer protect nickel during long-term shutdown conditions in a single cell.²⁷ However, there are still much fewer studies on the long-term stability of catalysts in complete AWE cells under frequent startup-shutdown conditions compared to the conventional three-electrode system, as shown in Table S1.

To address this gap, we investigated the impact of reverse current on the degradation of a Ru electrocatalyst for the hydrogen evolution reaction (HER) and LaNiO_3 for the OER in a single cell for water splitting. The cell was equipped with a reversible hydrogen electrode (RHE) as a reference electrode (Figure 1c). Ru electrocatalysts show one of the highest HER activities in alkaline conditions,^{28–33} but there has been a lack of detailed studies on the stability of Ru-based cathodes under dynamic on/off operating conditions. Thus, long-term stability tests were performed to measure the potentials of both the anode and cathode in each on/off cycle by using a synchronized measurement protocol with dual channels.

By exploring various combinations of anode and cathode materials, we identified that the ratio of the anode and cathode's double-layer capacitances is a crucial parameter that governs the changes in potential upon shutdown. Our findings demonstrate that the Ru cathode can be stabilized by carefully tuning its double-layer capacitance to balance it with that of the LaNiO_3 anode. This work provides new insights that could be used for constructing active and stable electrodes for AWE under the fluctuating conditions of RESs.

METHODS

Chemicals. Ni foam and Pt wire were purchased from Nilaco Corporation, and Ni felt (NF) was purchased from

Nikko Techno Corporation. Pt/C gas diffusion electrodes with Pt (0.5 mg cm⁻²) were purchased from Chemix. Hg/HgO (1 M NaOH) reference electrodes were purchased from BAS Inc. Other chemicals were purchased with the following purities from Fujifilm-Wako unless otherwise specified: HCl (35–37%), EtOH (≥99.5%), potassium hydroxide (KOH) (≥85%), nickel(II) nitrate hexahydrate [Ni(NO₃)₂ · 6H₂O] (≥98.0%), nickel chloride hexahydrate [NiCl₂ · 6H₂O] (≥98.0%), ammonium chloride (NH₄Cl) (≥99.5%), lanthanum(III) acetate sesquihydrate [La(CH₃COO)₃ · 1.5H₂O] (Thermo Scientific Chemicals, 99.9%), and ruthenium(III) chloride hydrate [RuCl₃ · xH₂O] (Sigma-Aldrich). All chemicals were used as received. Zirfon Perl UTP 500+ separators were purchased from Agfa and used as the diaphragms.

Electrodeposition of Ru on Ni Felt. The NF substrate was sonicated in ethanol, 10 wt % HCl, and ultrapure water for at least 5 min each and dried at room temperature. Electrodeposition was performed using a 15 mL bath of a 10 mM RuCl₃ solution. The NF was used as the working electrode with an area of 1 cm² immersed in the solution, and a carbon rod was used as the counter electrode. Ru was electrodeposited on the NF at a constant current density of −100 mA cm⁻² for 6 min to obtain the Ru/NF electrode.

Synthesis of LaNiO₃. LaNiO₃ was synthesized using a previous protocol reported by Tsukada et al.³⁴ NF (2.0 cm × 8.0 cm) was washed with acetone, 10% HCl, and ultrapure water under sonication for 5 min each. An aqueous solution containing 0.2 M La(CH₃COO)₃ · 1.5H₂O and 0.2 M Ni(NO₃)₂ · 6H₂O was used as a precursor solution. The NF was dipped into the precursor solution for 1 min, followed by calcination in air at 600 °C for 10 min. This process was repeated 16 times before a final calcination in air at 600 °C for 1 h to obtain the LaNiO₃/NF electrode.

Synthesis of Porous Ni and Porous NiRu. Porous Ni was synthesized by dynamic hydrogen bubble-template electrodeposition, which can form a porous structure using H₂ bubbles that are generated during the electrodeposition process.^{44,45} NF substrate was used as a working electrode after sonication in ethanol, 10% HCl, and water for 5 min each. The electrodeposition solution contained 0.20 M NiCl₂ and 2.0 M NH₄Cl. The porous Ni electrocatalyst was electrodeposited at a high current density of −1 A cm⁻² for 10 min (chronopotentiometry (CP)) to obtain porous Ni/NF.⁴⁶ For the NiRu electrocatalyst, the electrodeposition solution contained 0.10 M NiCl₂, 2.0 M NH₄Cl, and 0.01 M RuCl₃. The electrodeposition was carried out by applying 8 cycles of −1 A cm⁻² for 1 min and 100 mA cm⁻² for 30 s. A carbon rod was used as the counter electrode in each case. This process was used to obtain the porous RuNi/NF electrode.⁴⁶

Characterization. X-ray photoelectron spectroscopy (XPS) measurements were conducted with a JEOL JPS-9030 using an Al anode at 300 W, 12 kV, and 25 mA. All acquired data were calibrated using C 1s at 284.6 eV. Inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements were conducted with the Thermo iCAP PRO series. Scanning electron microscopy (SEM) images were obtained with a JEOL JSM IT-800. X-ray diffraction (XRD) patterns were recorded with a Rigaku MiniFlex X-ray diffractometer. Operando Raman spectra were recorded with a Jasco RMP-510 and a CCD camera. The excitation wavelength was 532.048 nm. The working electrode (LaNiO₃/NF) was immersed in 7 M KOH electrolyte at room temperature for operando Raman spectra measurement.

Platinum wire and Hg/HgO (1 M NaOH) were also immersed in the electrolyte as a counter electrode and reference electrode. The LaNiO₃/NF working electrode was first activated by applying 1 A cm⁻² for 1 h in 7 M KOH at 353 K before Raman spectroscopy measurements.

Electrochemical Tests in a Conventional Three-Electrode System. All electrochemical measurements were carried out using a 16-channel research-grade potentiostat system (VMP3; BioLogic Science Instruments). A polymethylpentene cell with high alkalinity tolerance (BAS Inc.) and a three-electrode configuration was immersed in an aluminum bead bath to keep the electrolyte temperature at 80 °C. O₂ and H₂ were supplied for the OER and HER measurements, while Ar gas was used during double-layer capacitance (C_{dl}) measurements. All working electrodes were sealed with poly(tetrafluoroethylene) (PTFE) tape to secure an effective geometric area of 1 cm². HER and OER polarization curves were obtained by applying a constant current of 1 A, 0.8 A, 0.6 A, 0.4 A, 0.2 A, 0.1 A, and 10 mA for 10 min each in 80 °C 7 M KOH solution. Solution resistance was measured by electrochemical impedance spectroscopy (EIS) in a frequency range of 0.1 Hz–200 kHz. A Pt coil and Ni foam were used as the counter electrode for OER and HER measurements, respectively, while Hg/HgO (1 M NaOH) was used as the reference electrode. The following equation was used to convert the recorded potentials to the RHE scale:

$$E_{\text{RHE}} = E_{\text{meas}} + E_{\text{Hg/HgO}}^0 + 0.0591 \text{ pH}$$

A value of $E_{\text{Hg/HgO}}^0 + 0.0591 \text{ pH}$ was determined through experimental calibration (Figure S1). The calibration was carried out by obtaining the current–potential curve of the Pt coil in H₂-saturated 7 M KOH solution at 80 °C via scanning cyclic voltammograms at 1 mV s⁻¹. The OER overpotential (η) was calculated according to the following equation

$$\eta = E_{\text{RHE}} - E_{\text{H}_2\text{O}}^0$$

The thermodynamic water splitting potential at 80 °C $E_{\text{H}_2\text{O}}^0$ was calculated by an empirical equation of;⁴⁷

$$E_{\text{H}_2\text{O}}^0 = 1.229 - 0.9 \times 10^{-3}(T - 298.15)$$

C_{dl} values were evaluated in Ar-purged 7 M KOH solution at 80 °C after HER/OER activity tests. The cyclic voltammetry (CV) scanning range was −0.550 to −0.350 V vs Hg/HgO for Ru and porous NiRu electrodes. For the LaNiO₃ electrocatalyst, the CV range was 0.066 to 0.266 V vs Hg/HgO. The scan speeds for the Ru and LaNiO₃ electrodes were 50, 40, 30, 20, 10, and 5 mV s⁻¹. For the porous Ni electrode and NF, the CV range was −0.130 to 0.070 V vs Hg/HgO. Faster scan speeds of 500, 400, 300, 200, 100, and 50 mV s⁻¹ were chosen for the porous Ni electrode and NF substrates.

Single-Cell Setup for Reverse Current Measurement and Stability Test. The single-cell electrolyzer had a geometric area of 1 cm² and consisted of a platinum-coated titanium flow plate as the anode and a carbon flow plate with an internal RHE reference electrode as the cathode. The detailed electrode setup is shown in Figure S2. The RHE reference electrode was electrically isolated from the cathode flow plate by a PTFE seal, and H₂ gas was introduced with a flow rate of 5 mL min⁻¹.

The Zirfon Perl UTP 500+ diaphragm was cut to a size of 3 × 3 cm to ensure contact between the reference electrode and the diaphragm. Thus, the electrocatalyst and reference

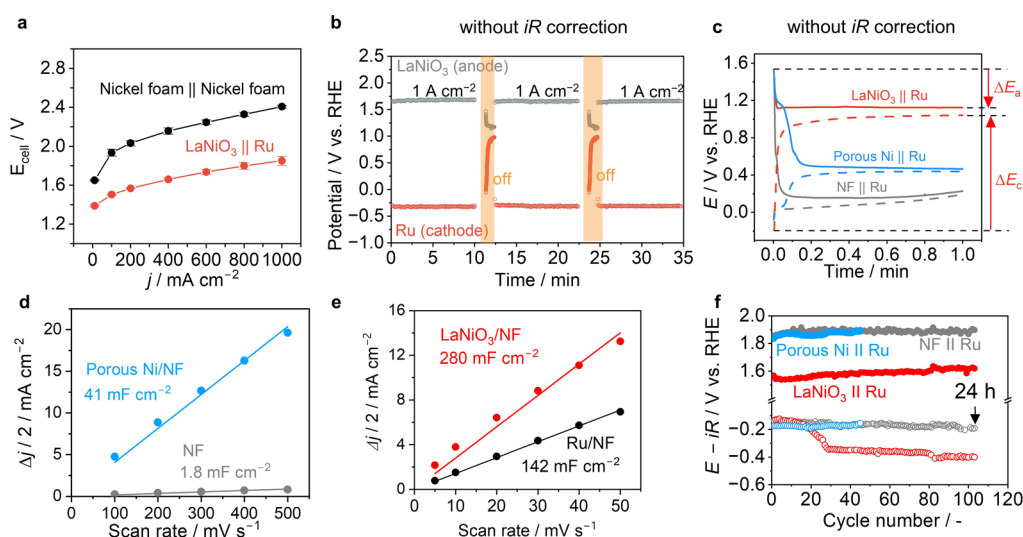


Figure 2. (a) Cell voltage at various current densities, (b) potential of cathode and anode upon shutdown, (c) reverse current density upon shutdown, (d, e) C_{dl} values for various electrodes, and (f) stability test with on/off cycle at 1 A cm^{-2} (open symbol: cathode, closed symbol: anode).

electrode were ionically connected through 7 M KOH that had permeated into the diaphragm. The electrolyte tanks and cell were heated to 80°C , and the temperature behind the reaction field was monitored by a temperature controller with a thermocouple. The 7 M KOH electrolyte was continuously supplied to the anode and cathode flow field from two separate electrolyte tanks at 15 mL min^{-1} .

The synchronization protocol for the reverse current measurement is shown in Figure 1d,e. Two channels were connected to the cell at the same time: one was directly connected to the current collector, while a 10-ohm ceramic resistor connected the second channel to the cell. The reverse current through the resistor and cell was measured by using the second channel via chronoamperometry (CA).

RESULTS

Ru and LaNiO_3 were synthesized, and their HER and OER performance was assessed by CP. The results are shown in Figure S3. The synthesized Ru catalyst required low overpotentials of 32, 59, and 113 to deliver current densities of 10, 100, and 1000 mA cm^{-2} . The as-synthesized LaNiO_3 catalyst demonstrated excellent OER activity with low overpotentials of 160, 218, and 304 mV to deliver current densities of 10, 100, and 1000 mA cm^{-2} in 7 M KOH at 80°C . Additionally, XRD results of the as-synthesized LaNiO_3 show peaks associated with perovskite LaNiO_3 (Figure S4).

Overall, alkaline water splitting was performed with a single cell using bare nickel foam and the Ru cathode and LaNiO_3 anode. As shown in Figure 2a, the cell voltage was 1.85 V at a high current density of 1 A cm^{-2} , which is comparable to state-of-the-art performance in overall AWE. As a comparison, a much higher cell voltage of 2.4 V was observed at 1 A cm^{-2} when bare nickel foam was used. The reverse current was investigated using the synchronization protocol (Figure S2d,e). Figure 2b shows the measured potential of the Ru cathode and the LaNiO_3 anode, respectively, during on/off operation. While the potentials of the cathode and anode are constant during normal operation (on condition), their potential drastically changes within just the first 30 s of shutdown (off

condition) and reaches the same rest potential ($E_{\text{rest}} \approx 1.0 \text{ V}_{\text{RHE}}$ in this case).

In Figure 2c, the electrode potential upon shutdown is shown when the anode was changed from LaNiO_3 to a porous Ni electrodeposited on NF and bare NF, while the cathode was fixed to Ru. When using the LaNiO_3 anode, the potential of the cathode changed drastically to approximately 1.0 V (ΔE_c), while the potential of the LaNiO_3 anode showed little change (ΔE_a). Surprisingly, the opposite trend was observed when porous Ni and bare NF were used as the anode. The rest potential (where the potentials of the anode and cathode become equal) decreased to around 0.4 and 0.2 V when Ru was combined with these anodes. The reverse current started at approximately 130–140 mA cm^{-2} in all cases, but the rate at which it decreased was greatest with the bare NF and slowest with the LaNiO_3 (Figure S5).

We focused on the electrode's double-layer capacitance C_{dl} to explain this trend because it can be proportional to the total charge accumulation, which leads to the reverse current. As shown in Figure 2d,e, C_{dl} varied widely between the tested anodes (bare NF: 1.8 mF cm^{-2} , porous Ni: 41 mF cm^{-2} , LaNiO_3 : 286 mF cm^{-2}), while the Ru cathode's value was maintained (137 mF cm^{-2}). The potential of the Ru cathode changed drastically when it was combined with LaNiO_3 because the C_{dl} of LaNiO_3 is almost twice as high as that of Ru. On the other hand, ΔE_c was small when using bare NF because it has a much smaller C_{dl} than Ru.

The stability test with dynamic on and off cycles in a single cell revealed that the Ru cathode activity deteriorated from $-0.13 \text{ V}_{\text{RHE}}$ to $-0.34 \text{ V}_{\text{RHE}}$ in just 30 cycles when combined with LaNiO_3 (Figure 2f). However, it was stable for more than 100 cycles when using bare NF. SEM images of the electrodes from after the stability test show that there was almost no Ru left on the NF substrate when it was combined with LaNiO_3 (Figure S6). The Zirfon separator turned black, which was most likely due to leftover Ru that had adhered to it. When the bare NF anode was used, a uniform layer of Ru was clearly observed on the NF substrate with little detachment after the 24 h stability test.

To gain more insight into the Ru degradation, a stability test was performed with on/off cycles to simulate reverse current using the ADT protocol in a three-electrode system (Figure S7).²² The ADT protocol involved CP at 1 A cm⁻² for 10 min (on condition), followed by solution-resistance measurement by EIS. Linear sweep voltammetry (LSV) was then performed at 100 mV s⁻¹ toward the respective resting potentials (E_{rest}) to simulate power fluctuations, after which the potential was held for 1 min during CA to emulate reverse current conditions. Significant Ru degradation was observed when E_{rest} was higher than 1.0 V, which was similar to the degradation observed in a single cell (Figure 3a). The reverse current was almost twice as

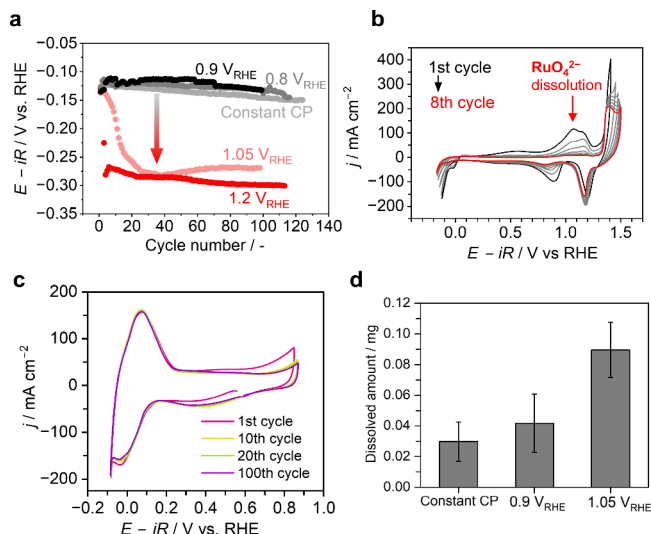
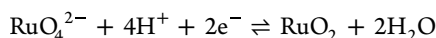


Figure 3. (a) Stability test of Ru cathode in 7 M KOH at 80 °C with various rest potentials E_{rest} , CV of Ru in Ar-purged 7 M KOH at 80 °C with the range between (b) -0.1 and 1.41 V_{RHE} and (c) -0.1 and 0.9 V_{RHE}, respectively, and (d) amount of Ru dissolved in the electrolyte after 24 h stability test after CV with various E_{rest} .

large at $E_{\text{rest}} = 1.05$ V_{RHE} as that at $E_{\text{rest}} = 0.9$ V_{RHE} (Figure S7b,c). At $E_{\text{rest}} = 1.05$ V_{RHE}, the initial reverse current decreased from 140 mA cm⁻² (first cycle) to 35 mA cm⁻² (100th cycle). In contrast, the initial reverse current was almost constant at 85 mA cm⁻² for 100 cycles. The discharge was calculated by integrating the reverse current over time, as shown in Figure S7f. The discharge became smaller as the cycle number increased, which indicated a decrease in the amount of catalysts on the electrode surface. To gain more information about the degradation behavior, CV was performed with Ru in 7 M KOH at 80 °C with 8 repeated scans between -0.1 V_{RHE} and $+1.41$ V_{RHE} (Figure 3b). During the first cycle, a large oxidation peak appears at about 1.0 V_{RHE}, which indicates the oxidation of Ru⁴⁺ to Ru⁶⁺. This corresponds to the formation of ruthenate (RuO₄²⁻), which is soluble in an alkaline solution.^{35–37}



However, during OER at higher potentials, further oxidation might occur and produce highly oxidized Ru species ($>6+$), which is not stable in an alkaline solution.^{36,37} As shown in Figure 3b, the redox peaks of the Ru species decreased significantly as the cycle number increased, which indicated corrosion of the Ru layer on the Ni substrate. Holmin et al. also showed that anodic polarization after HER causes

oxidation of RuO(OH)₂ into RuO₄²⁻.³⁸ Interestingly, the Ru electrode was stable for 100 cycles when CV was performed with a narrower range from -0.1 V_{RHE} to $+0.9$ V_{RHE} (Figure 3c).

The ICP results of the electrolytes after 24 h of dynamic stability testing showed a 3 times higher ruthenium dissolution at $E_{\text{rest}} = 1.05$ V_{RHE} compared to the cases of constant CP and $E_{\text{rest}} = 0.9$ V_{RHE} (Figure 3d). This result further indicates that the Ru electrode is not stable if its potential becomes higher than 1.0 V_{RHE} because it oxidizes into ruthenate species and dissolves in the alkaline electrolyte. Notable agglomerations and exposed nickel surfaces were observed in the SEM image obtained after the stability test at $E_{\text{rest}} = 1.05$ V_{RHE} (Figure S8). XPS was employed to gain insight into the surface electronic structure of Ru after applying 0.9 V_{RHE} and 1.2 V_{RHE} (Figure S9). The Ru 3p peak indicates the presence of almost metallic Ru after application of 0.9 V_{RHE}. In contrast, the Ru 3p peak shifted to higher binding energy and became more like the RuO₂ peak after applying 1.2 V_{RHE}.⁴⁸

The effects of E_{rest} were also investigated in a three-electrode system with a LaNiO₃ electrode (Figures 4 and S7). The same

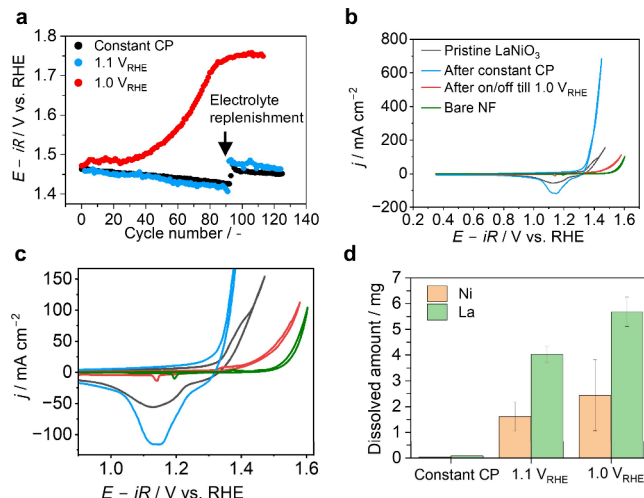


Figure 4. (a) Stability test of LaNiO₃/NF with various rest potentials E_{rest} , (b) CV of LaNiO₃ and bare NF in Ar-purged 7 M KOH in 80 °C, where (c) is enlarged figure of (b), and (d) amount of Ni and La dissolved in the electrolyte after the 24 h stability test.

ADT protocol was used (Figure S7a). The LaNiO₃ electrode was stable in the constant-CP stability test, and when E_{rest} was 1.1 V_{RHE}, but significant deactivation was observed when E_{rest} was 1.0 V_{RHE}. The reverse current was almost twice as large at $E_{\text{rest}} = 1.0$ V_{RHE} as that at $E_{\text{rest}} = 1.1$ V_{RHE} (Figure S7d,e). At $E_{\text{rest}} = 1.0$ V_{RHE}, the initial reverse current decreased from over 400 mA cm⁻² (first cycle) to less than 30 mA cm⁻² (100th cycle). CV was performed for each electrode after 24 h of dynamic stability testing, as shown in Figure 4b,c. Redox peaks near 1.15 V_{RHE} and 1.4 V_{RHE} were observed for every sample and were assigned to the NiOOH/Ni(OH)₂ (Ni³⁺/Ni²⁺) redox couple.^{39–41} The LaNiO₃ electrode demonstrated a much larger reduction peak than the pristine LaNiO₃ electrode after the 24 h stability test because of catalyst activation at anodic OER potential, which was most likely due to the well-known surface reconstruction of perovskite for OER.⁴²

After on/off cycling at $E_{\text{rest}} = 1.0$ V_{RHE}, the LaNiO₃ electrode showed a small reduction peak that was almost identical to that

of bare NF. This indicates that a significant number of catalytic sites of Ni were lost during on/off cycling. The observed deactivation is mostly due to mechanical peeling of LaNiO_3 from the NF substrate at high current density, as there was a large amount of precipitated black powder in the electrolyte. This is supported by the significant amount of Ni and La found in the ICP analysis of the electrolyte after on/off cycling, as shown in Figure 4d. Lee et al. reported that the incomplete reduction of the OER active phase $\gamma\text{-NiOOH}$ to $\beta\text{-Ni(OH)}_2$ results in significant degradation during many redox cycles.⁴³ Frequent on/off cycling could trigger this irreversible redox if the E_{rest} value is as low as 1.0 V and could also induce catalyst peeling due to bubble generation at a high current density. Almost complete peeling of the catalyst layer from the NF substrate was observed in the SEM image obtained after the stability test at $E_{\text{rest}} = 1.0 \text{ V}_{\text{RHE}}$ (Figure S10). In comparison, more catalyst was present as E_{rest} increased to 1.1 V, and needle-like catalyst was distributed uniformly on the electrode after only constant CP. To gain insight into more direct evidence related to the reduction of $\gamma\text{-NiOOH}$ to $\beta\text{-Ni(OH)}_2$, we conducted in situ operando Raman spectroscopy measurements in 7 M KOH at room temperature. First, the potential was set to 1.4 V_{RHE} for 10 min before 1.1 V_{RHE} . Then, the potential was set back to 1.4 V_{RHE} for 10 min, after which 1.0 V_{RHE} was applied. Two peaks at around 475 and 555 cm^{-1} were observed at 1.4 V_{RHE} , which correspond to the vibration of NiOOH (Figure 5a,b).^{49,50} The NiOOH peak intensity

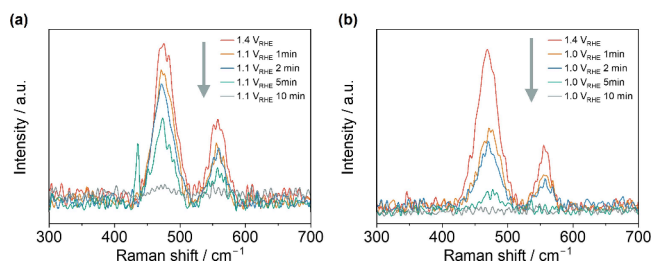


Figure 5. Operando Raman spectroscopy of LaNiO_3/NF in 7 M KOH at room temperature. (a) Applied potential of 1.1 V_{RHE} . (b) Applied potential of 1.0 V_{RHE} .

decreased much faster when 1.0 V_{RHE} was applied, and the NiOOH peaks completely disappeared after 10 min. In contrast, a more gradual change was observed when 1.1 V_{RHE} was applied, and very small NiOOH peaks were still observable after 10 min. This result suggests that the reduction of $\gamma\text{-NiOOH}$ to $\beta\text{-Ni(OH)}_2$ happens much faster when E_{rest} equals 1.0 V_{RHE} while it is more gradual when E_{rest} equals 1.1 V_{RHE} . Thus, rapid LaNiO_3 degradation was observed when 1.0 V_{RHE} was applied during the accelerated stress test.

Then we tested the stability of $\text{LaNiO}_3 \parallel \text{Ru}$ in a single-cell configuration. It was hypothesized that the Ru cathode could be stabilized if its potential is kept below 1.0 V, which we tested by designing a porous NiRu cathode with a very high double-layer capacitance of 365 mF cm^{-2} , comparable to that for LaNiO_3 (Figure 6a). As shown in Figure 6b, the porous NiRu had excellent stability even after almost 250 on/off cycles for 3 days when combined with the LaNiO_3 anode. As expected, its potential was successfully maintained below 0.5 V_{RHE} upon shutdown, which is below the dissolution threshold due to its higher double-layer capacitance than that of the Ru cathode (Figure 6d). The CV of as-made porous NiRu also shows Ru^{6+} formation at around 1.0 V_{RHE} , indicating the

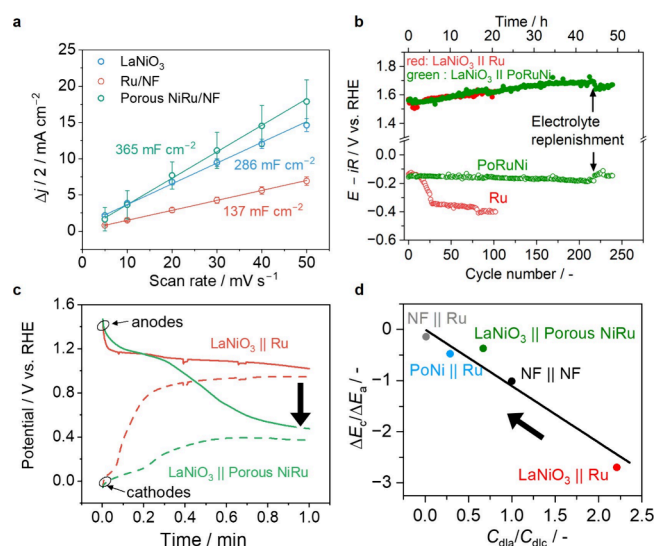


Figure 6. (a) Current density associated with C_{dl} values as a function of scan rates, (b) stability test of LaNiO_3 and as-obtained or porous Ni substrate with on/off cycles at 1 A cm^{-2} , (c) relationship between the C_{dl} ratio and potential change ratio, and (d) potential of anode and cathode measured during shutdown condition.

dissolution of Ru (Figure S11). This suggests that the excellent stability of porous NiRu is due to the regulated rest potential during shutdown conditions, not due to other factors. Regarding the LaNiO_3 anode, this test did not cause much deactivation, while apparent quicker deactivation was observed in the three-electrode system (Figure 4a). The difference may come from the operation where quick LSV (100 mV s^{-1}) was conducted to E_{rest} right after 1 A cm^{-2} CP in the three-electrode system compared to gradual potential relaxation via shutdown operation (open circuit condition). The forced reduction of Ni species in LaNiO_3 as well as the Ni substrate at $\sim 1.0 \text{ V}_{\text{RHE}}$ may induce mechanical shock, leading to severe detaching and consequent deactivation. As expected, when the LSV scan rate was lowered to 10 mV s^{-1} , the degradation rate of LaNiO_3 was 3 times lower when compared to 100 mV s^{-1} in the three-electrode system (Figure S12).

As discussed previously (Figure 2), the reaching potential of a single cell is strongly influenced by the capacity of the respective electrode substrates in a single-cell configuration. Indeed, a linear correlation was observed between the ratio of potential shifts ($\Delta E_{\text{a}}/\Delta E_{\text{c}}$ designated in Figure 2c) and C_{dl} ratios ($C_{\text{dlc}}/C_{\text{dla}}$) (Figure 6d), which confirmed that C_{dl} reasonably represents the charge accumulation and resultant resting potential (the subscripts “a” and “c” indicate the anode and the cathode, respectively). An increase in cathode capacitance shifts the reaching potential in the negative direction, whereas an increase in anode capacitance shifts it in the positive direction, reflecting opposite trends. By combining the knowledge of the electrodes’ chemical nature, reverse current behavior with potential control is possible for improved stable performance operation. In this case, chemical dissolution of Ru was avoided by keeping the reaching potential more negative than the dissolution potential. Further investigation is, however, still necessary to improve the strong mechanical binding of an oxide, such as LaNiO_3 , to the metallic substrate by immense perturbation of the potential sweep. In summary, this study offers novel insights that significantly advance our understanding and control of retrogressive current

behavior and resultant durability upon on and off cycles in the AWE system and beyond.

CONCLUSIONS

This study characterized the degradation of Ru cathodes and LaNiO₃ anodes for an AWE single cell under reverse current generated during dynamic on/off operation by ADTs. Electrochemical measurements were effectively utilized to compare CV in a conventional three-electrode system to get more insights into each electrode. Our synchronization protocol enabled the investigation of reverse current in a more practical single cell, and the critical role of C_{dl} in changes in the electrode potential during shutdown was clarified. Balancing the C_{dl} values of the anode and cathode mitigated unfavorable Ru oxidation, thereby prolonging the cathode's lifespan for AWE operation. As long as the Ru potential remains below its dissolution threshold ($\sim 1.0 V_{RHE}$), stability can be maintained. These findings underscore the critical role of charge capacity matching in preventing degradation from redox imbalance. Adjusting C_{dl} offers one of the practical means of tuning the resting potential under closed-circuit conditions. The electrolyzer lifetime could be increased based on knowledge of the redox properties for both the cathode and anode and by controlling the rest potential.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.5c04643>.

Detailed description of synchronization protocol, photographs of experimental setup, SEM images of electrodes after ADT, and measured reverse current and discharge (PDF)

AUTHOR INFORMATION

Corresponding Author

Kazuhiro Takanabe – Department of Chemical System Engineering, School of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan; orcid.org/0000-0001-5374-9451; Email: takanabe@chemsys.t.u-tokyo.ac.jp

Authors

Tengisbold Gankhuyag – Department of Chemical System Engineering, School of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan

Keisuke Obata – Department of Chemical System Engineering, School of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan; orcid.org/0000-0003-3544-9505

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.jpcc.5c04643>

Author Contributions

T.G. performed all electrochemical experiments and analyses. All the authors wrote the manuscript, and K.T. obtained the funding and supervised the project.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful to the following for their support: GteX Program Japan (Grant Number JPMJGX23H2) and the MEXT Program: Data Creation and Utilization-Type Material Research and Development Project (Grant Number JPMXP1122712807). T.G. acknowledges the scholarship support from Iwatani Naoji Foundation.

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