

Article

Restoring the Performance of Polymer Electrolyte Membrane Water Electrolysis Cells by Immersion in Strong and Weak Acids Without Cell Disassembly

Taiga Goto , Pyae Pyae Shwe Sin  and Kensuke Nishioka * 

Faculty of Engineering, University of Miyazaki, Miyazaki 889-2192, Japan;
hn21127@student.miyazaki-u.ac.jp (T.G.); z322t03@student.miyazaki-u.ac.jp (P.P.S.)

* Correspondence: nishioka@miyazaki-u.ac.jp

Abstract

Hydrogen production via polymer electrolyte membrane (PEM) water electrolysis has attracted considerable attention as a promising technology to store renewable electricity and combat global warming. Although PEM water electrolyzers can produce high-purity hydrogen at high current densities, the use of low-purity water leads to device degradation because metal ions from the water are deposited on the membrane, thereby increasing its resistance and operating voltage. In this study, an in-situ recovery method was developed, in which degraded PEM water electrolysis cells were chemically treated without disassembly. Cells after degradation were subjected to a 24-h chemical treatment with either a strong acid (1.0 mol/L nitric acid) or a weak acid (12.9 and 1.0 mol/L phosphoric acid), followed by the supply of ultrapure water for 72 h. Recovery was evaluated using cell voltage measurements, while scanning electron microscopy (SEM)-dispersive X-ray spectroscopy (EDX) and inductively coupled plasma (ICP) analyses were performed to investigate membrane morphology, elemental distributions, and metal ion removal. Among the tested acids, 12.9 mol/L phosphoric acid showed the highest voltage recovery performance, achieving a 90% recovery ratio immediately after treatment (0 h). Moreover, a comparison of the voltage recovery ratios at 1 h post-immersion suggests that higher hydrogen ion concentrations are more effective for the recovery of degraded PEMs. These findings demonstrate that in-situ acid treatment can restore the performance of contaminated PEM water electrolyzers without disassembly and may provide a practical approach for extending cell lifetime and reducing maintenance requirements.

Keywords: polymer electrolyte membrane electrolysis; strong acids; weak acids; hydrogen ions; performance restoration; green hydrogen



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1. Introduction

Due to its intermittent nature, renewable electricity from wind and photovoltaic systems may be in surplus [1–6], and efficient technologies are needed to convert and store excess electrical energy for later use [7–10]. Hydrogen is a promising medium for storing such excess electrical energy [11,12]. There are four primary methods for hydrogen production via electrolysis: alkaline water electrolysis (AWE), solid oxide electrolysis (SOE), microbial electrolysis cells (MECs), and polymer electrolyte membrane (PEM) water electrolysis [13–20]. Compared to the other three methods, PEM water electrolysis offers several distinct advantages. It is considered highly safe, as it operates at relatively low

temperatures (20–80 °C) and high current densities (exceeding $2.0 \text{ A}\cdot\text{cm}^{-2}$), exclusively yielding high-purity ($\geq 99.99\%$) hydrogen and oxygen [13,21,22]. Compared to AWE, PEM technology exhibits superior tolerance to fluctuating power inputs and minimal performance degradation during shutdowns, making it highly suitable for integration with intermittent power sources such as photovoltaics [23–25].

Nevertheless, PEM water electrolysis faces significant challenges that are primarily related to the materials involved. The core of a PEM cell is the membrane electrode assembly (MEA), which incorporates a cation-exchange membrane. The electrolyte membrane, typically Nafion, is thermally stable up to 280 °C, which is the decomposition temperature of its sulfonic acid groups [26,27]. This necessitates the use of expensive precious-metal catalysts such as platinum and iridium as electrodes [28,29], because nonprecious metals are susceptible to rapid oxidation and dissolution in solid electrolytes under such corrosive acidic conditions. Moreover, stable long-term hydrogen production demands ultrapure water, which is relatively expensive [30,31]. In comparison, seawater and river water contain numerous metal ions and other substances [32]. The deposition of these metal ions and cations from the feed water onto the MEA increases membrane resistance and operating voltage, which in turn reduce the hydrogen generation efficiency and contributes to degradation of the water electrolyzer [33,34].

One attractive option is to restore the cell performance (i.e., reducing the cell voltage and increasing the hydrogen generation rate) after operating with low-purity water such as river water without replacing the MEA, because this approach could lead to significant cost savings. Researchers have investigated the effects of metal ion contaminants in the feed water on the degradation of water electrolysis cells. The primary cationic species that adversely affect PEM electrolysis are reported to be Fe^{3+} , Mg^{2+} , Ca^{2+} , Cu^{2+} , and Na^{+} [35–48]. Other researchers developed processes for recycling the expensive noble-metal catalysts and achieved a high recycling rate for Nafion membranes via sulfuric acid treatment [49]. Some studies have demonstrated that the cell voltage can be reduced by switching the feed water back to ultrapure water and operating the cell at a constant current after degradation. In one approach, the degraded MEA was removed from the cell, treated with nitric acid, reassembled into the cell, and operated using ultrapure water to restore its performance [50]. Other researchers reported partial recovery of cell performance using only deionized (DI) water, thereby avoiding harsh acid treatments [51]. However, almost all reported systematic acid treatments of PEM water electrolyzers required cell disassembly. Moreover, the relative effects of acid strength, acid concentration, and interactions between acid anions and deposited cations remain unclear.

In this study, we developed an in-situ recovery process using nitric acid (1.0 mol/L) and phosphoric acid at two concentrations to lower the cell's operating voltage and restore the hydrogen production rate. This is distinct from previously reported ex-situ recovery approaches that require cell disassembly.

2. Materials and Methods

2.1. PEM Water Electrolysis Cell

The experiments were conducted using an EHC-070 water electrolyzer (Enoah Int., Toyota, Japan). Figure 1 illustrates the cell structure, which features porous feeders and compound electrode plates situated at both ends of the MEA. According to the manufacturer's specifications, the nominal operating voltage is 1.8–2.3 V at a current of 9.0 A. Replacement of the MEA is recommended if the voltage exceeds 3.0 V due to performance degradation. Although the maximum allowable current was 10 A, all voltage evaluations in this study were performed at 9.0 A to align with the manufacturer's specified operating criteria. The MEA had an active surface area of 11.34 cm^2 .

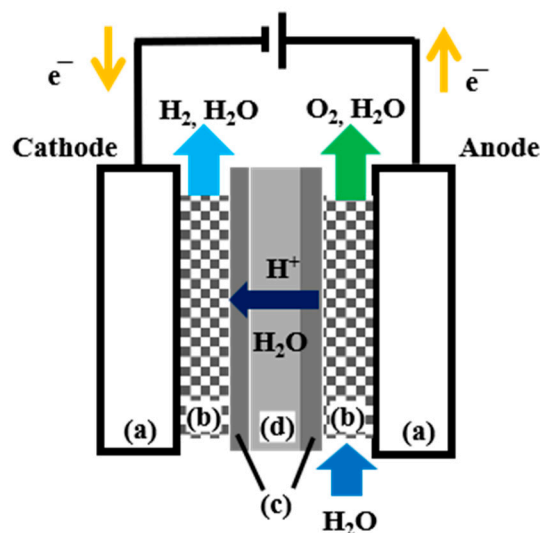
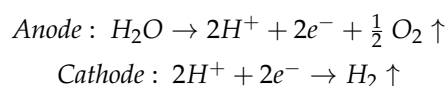


Figure 1. Configuration of the PEM water electrolysis cell including (a) compound electrode plates, (b) porous feeders, (c) catalyst electrodes, and (d) proton exchange membrane (MEA).

2.2. Experimental Setup

Figure 2 shows a schematic of the experimental setup. Water was supplied to the anode side of the cell at a rate of 1.5 mL min^{-1} using a peristaltic pump. During electrolysis, the following reactions occur at the anode and cathode, respectively [52]:



The produced hydrogen was dried using molecular sieves, and its flow rate was measured using a mass flow meter. The experiment was conducted at room temperature (25°C), and the cell was operated at a constant current of 9.0 A . The operating voltage of the cell and the voltage across the shunt resistor were measured and recorded over time using a memory Hi-Logger. The cell performance was characterized by three efficiencies: Faraday efficiency (η_f), voltage efficiency (η_V), and electrolysis efficiency (η_{EC}). The relationship among them is expressed by Equation (1) [53]:

$$\eta_{EC} = \eta_f \eta_V \quad (1)$$

The Faraday efficiency (η_f) was defined by the ratio of the actual electric charge (Q_{re}) to the theoretical electric charge (Q_{id}). Considering that Q_{re} is determined from the actual amount of hydrogen produced, N_H (mol), and that the production of 1.0 mol of H_2 consumes 2.0 mol of electrons, η_f can be expressed using Equation (2) [54]:

$$\eta_f = \frac{Q_{re}}{Q_{id}} = \frac{2FN_H}{It} \quad (2)$$

where F is the Faraday constant ($96,485 \text{ C mol}^{-1}$), I is the current applied during electrolysis (A), and t is the duration of current application (s). Given the operating voltage, E_{cell} , the voltage efficiency, η_V , was determined by Equation (3) based on the thermoneutral standard:

$$\eta_V = \frac{E_{th}}{E_{cell}} \quad (3)$$

where E_{th} is the thermoneutral voltage (1.48 V at 1 atm and 25 °C). Based on Equations (2) and (3), the operating voltage (E_{cell}) and hydrogen flow rate (N_H/t) were evaluated and used as the key performance indicators.

In this study, the theoretical hydrogen generation rate, H_{id} [mL/min], at an operating current of 9.0 A, was calculated using Equation (4):

$$H_{id} = \frac{9.0 [A]}{(F \cdot 2) \cdot 22.4 [l/mol] \cdot 60 \cdot 1000} \quad (4)$$

where F (the Faraday constant, 96,485 C mol⁻¹) corresponds to a theoretical hydrogen generation rate (H_{id}) of 62.6 mL/min. Figure 3 shows a flow diagram outlining the experimental procedure.

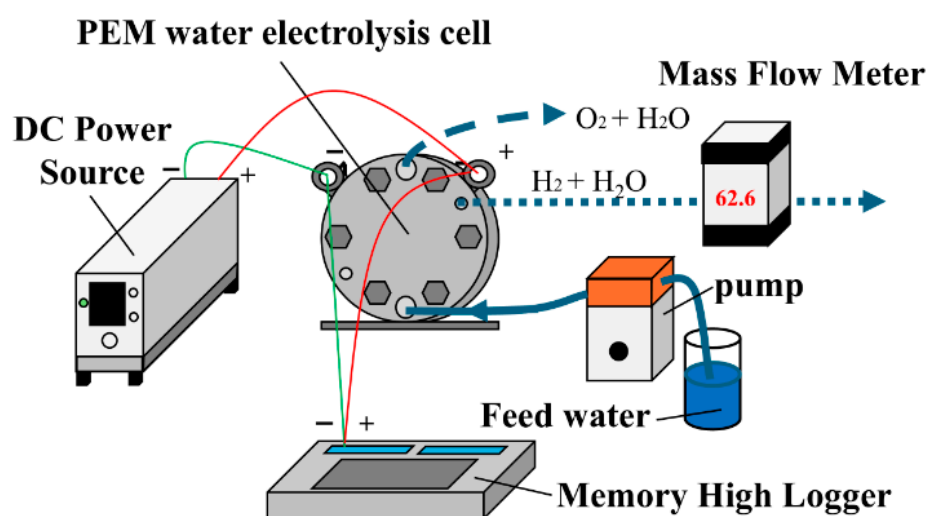


Figure 2. Schematic circuit diagram used in the experiment.

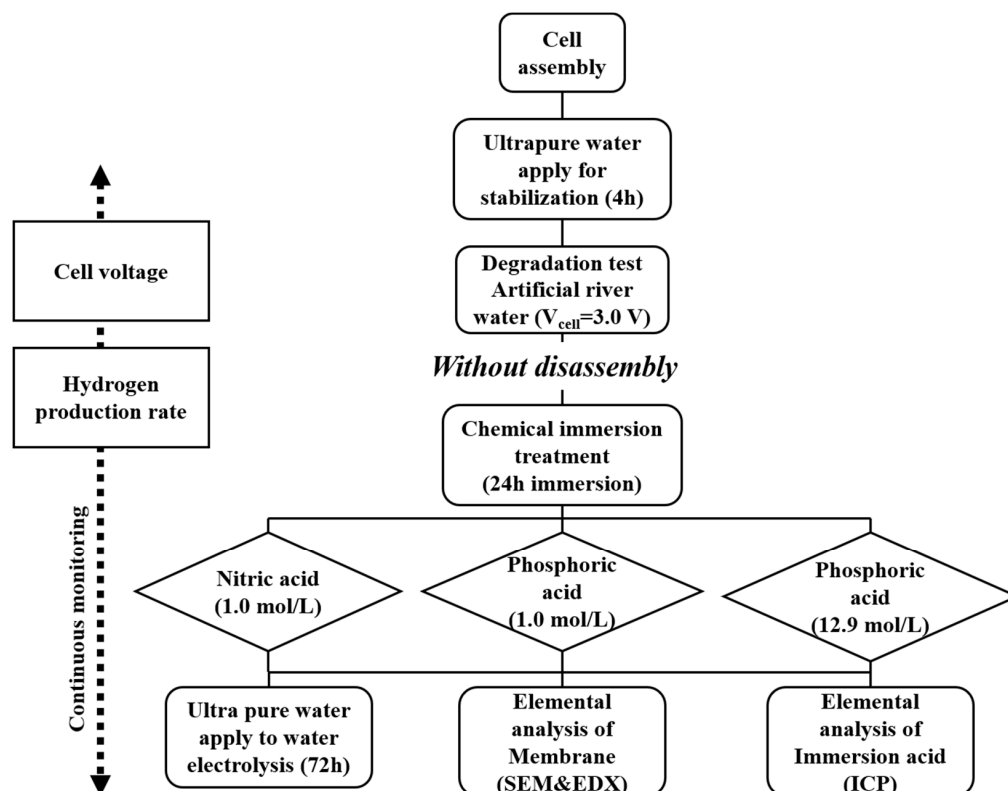


Figure 3. Experimental flow diagram of the degradation and recovery processes.

2.3. Cell Degradation Method

To stabilize the operating voltage, the water electrolysis cell was first operated with ultrapure water for 4 h. Then, the feed water was switched to artificial river water (see Table 1 for its composition), and electrolysis was continued until the operating voltage reached 3.0 V, which is the manufacturer's recommended threshold for MEA replacement. This step intentionally degraded the MEA. Degraded MEAs with and without the subsequent recovery process (described later) were analyzed using scanning electron microscopy (SEM, SU3500, Hitachi High-Tech, Tokyo, Japan) and energy-dispersive X-ray spectroscopy (EDX, EDAX Genesis-APEX2, Tokyo, Japan) for elemental analysis.

Table 1. Composition of the artificial river water.

Salt	Content (mg/L)
NaHCO ₃	48
CaSO ₄ ·2H ₂ O	30
MgSO ₄	30
KCl	2

2.4. Cell Restoration Method

The goal of the restoration procedure is to reduce the amount of metal ions deposited on the MEA during degradation, thereby lowering the operating voltage and restoring the hydrogen production rate. Following cell degradation using artificial river water, the current was turned off, and the cell was detached from the experimental setup. The desired acid solution was injected into the cell from the anode until it flowed through the cathode. The cell was then sealed with rubber tubing (Figure 4), and left for 24 h to ensure that the MEA was completely immersed in the acid solution. In a previous study, the cell was disassembled, and the degraded membrane was soaked in nitric acid for 24 h [50]. Therefore, the present study used a fixed soaking duration of 24 h to enable a direct comparison. The concentration of nitric acid was 1.0 mol/L nitric acid to match Ref. [50]. Because nitric acid is a strong acid and hazardous chemical, we tested phosphoric acid as a safer alternative because it is a trivalent and weaker acid. Two acid concentrations were used: 12.9 and 1.0 mol/L.

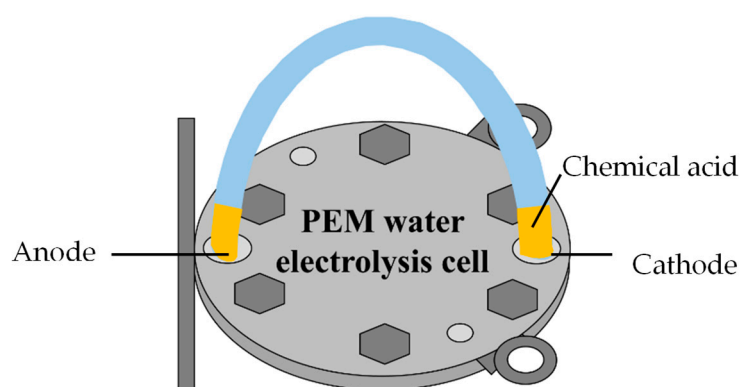


Figure 4. Schematic diagram of the restoration setup.

After soaking, the acid solution was flushed from the cell with ultrapure water. The cell was then reinstalled in the experimental setup, followed by electrolysis with ultrapure water for 72 h. During this 72-h period, the operating voltage and hydrogen generation rate were recorded continuously. The acid solutions flushed from the cells were collected for qualitative and quantitative analyses using an inductively coupled plasma (ICP) atomic emission spectrometer (ICPS-8100, Shimadzu, Kyoto, Japan) to determine the dissolution

of metal ions that had been deposited on the MEA during degradation. The measurement instruments used in this study had the following specifications: the DC power supply (PWR401L, KIKUSUI Electronics) had output accuracies of $\pm(0.03\%$ of reading +20 mV) for voltage and $\pm(0.1\%$ of reading +20 mA) for current; the mass flow meter (M-100SCCM-D, Alicat Scientific, Tucson, AZ, USA) had an accuracy of $\pm 0.8\%$ of reading $\pm 0.2\%$ of full scale (F.S.); the ICP-OES (ICPS-8100, Shimadzu, Kyoto, Japan) had a spectral resolution of 0.0045 nm; and the SEM had a spatial resolution of 3.0 nm. Elemental analysis was performed using an EDX system.

3. Results

3.1. Cell Degradation

Figure 5a shows the voltage profile of the cell as it degraded from the initial state until the voltage reached 3.0 V. The corresponding changes in the hydrogen generation rate are shown in Figure 5b. After switching from ultrapure water to artificial river water, the voltage rose sharply, reaching the recommended MEA replacement threshold of 3.0 V, as shown in Figure 5a. The average time required to reach this threshold was 6.6 ± 0.5 h ($n = 3$). Meanwhile, the average degradation rate for the hydrogen generation rate was $6.6 \pm 2.0\%$ ($n = 3$) in Figure 5b. These changes are likely due to metal ions replacing protons in the sulfonic acid groups in the MEA, altering the membrane structure and promoting hydrogen crossover. This allows hydrogen, which should only be released at the cathode, to permeate to the anode side [47,55,56]. Figure 5c shows an SEM image of the MEA cross-section and the EDX elemental analysis results. Figure 5d presents the weight percentage of each metal ion deposited on the MEA. Ca^{2+} and Mg^{2+} were particularly prevalent on the degraded MEA, accounting for 14.8% and 8.4% of the deposits, respectively. This suggests that their deposition was the primary cause of cell degradation. Due to the localized nature of the EDX analysis, these results should not be considered representative of the bulk membrane.

The preferential deposition of Ca^{2+} and Mg^{2+} among the four metal ions in the artificial river water was thought to be related to the cation-exchange selectivity of sulfonated polymers in the membrane. Cation exchange in Nafion generally favors divalent cations such as Ca^{2+} and Mg^{2+} over monovalent cations because of their stronger interaction with sulfonic acid groups [40,57], a trend that is consistent with the deposition behavior observed in the present study. Therefore, Ca^{2+} and Mg^{2+} undergo cation exchange more readily, leading to their greater deposition on the MEA and, consequently, becoming the main contributors to degradation.

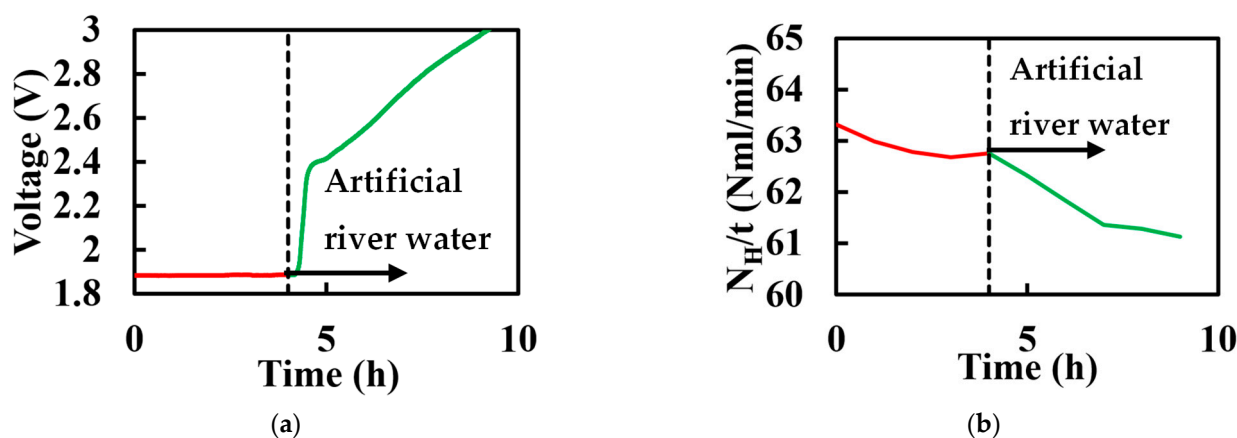


Figure 5. Cont.

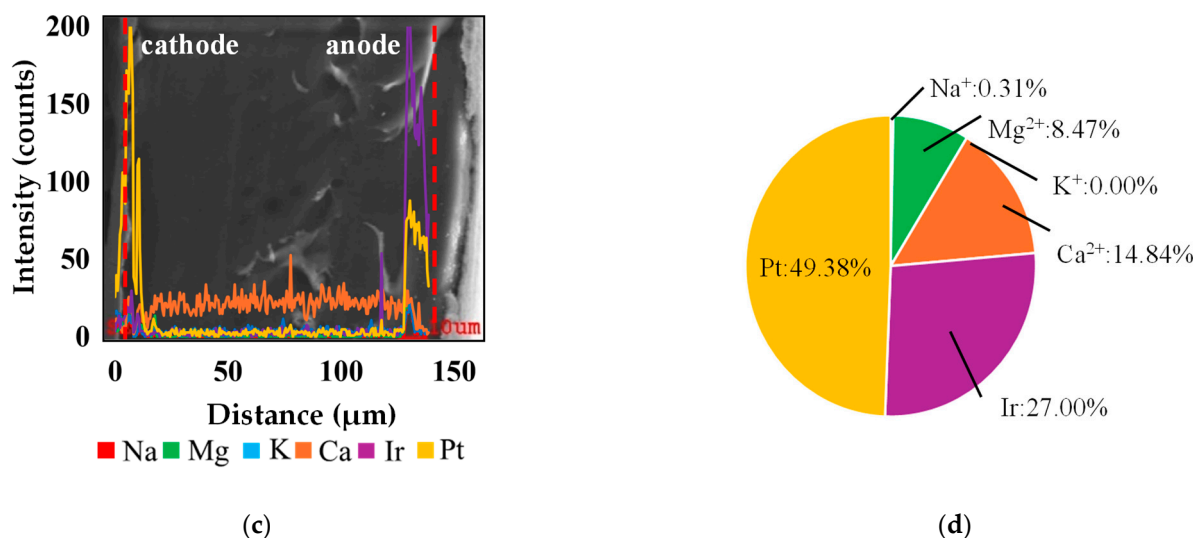


Figure 5. Degradation of the PEM cell during operation with artificial river water. (a) Cell-voltage profile after switching the feed water from ultrapure water to artificial river water. (b) The corresponding hydrogen production rate. (c) Representative cross-sectional SEM image and EDX line-scan profile of the degraded MEA. (d) Locally measured elemental weight percentages in the selected region for EDX analysis. These values are semi-quantitative and are not representative of the bulk MEA.

3.2. Effect Results of Nitric Acid Immersion

Figure 6a shows the voltage profile of the cell after immersion in 1.0 mol/L nitric acid for 24 h followed by operation with ultrapure water, as well as that from a previous study in which the degraded cell was operated with ultrapure water without immersion treatment [50]. While the voltage decline was similar between the two cases during the first 5 h post-immersion, the decline rate in the present study became significantly steeper after 20 h. The voltage recovery ratio after nitric acid immersion reached 89.5% after 24 h and $97.2 \pm 1.6\%$ (mean $\pm$ SD, $n = 2$) after 72 h, compared with 81.0% and $89.2 \pm 3.3\%$ (mean $\pm$ SD, $n = 2$) in the case without immersion, respectively. These results demonstrate that nitric acid immersion substantially accelerated the restoration of cell performance. The recovery ratio of hydrogen generation rate after 72 h was $96.0 \pm 2.5\%$ (mean $\pm$ SD, $n = 2$), slightly lower compared with $98.1 \pm 4.4\%$ (mean $\pm$ SD, $n = 2$) in case without immersion. Nevertheless, both treatments achieved hydrogen recovery ratios greater than 95%. Hence, nitric acid immersion primarily accelerated voltage recovery, whereas it maintained high hydrogen generation recovery but did not improve the final hydrogen recovery ratio compared with the case without acid immersion.

Furthermore, SEM-EDX analyses of the MEA cross-sections (Figure 6b) revealed a significant reduction in metallic deposits after nitric acid immersion compared with the degraded state. Figure 6c shows the weight percentage of each metal ion deposited on the MEA. The amount of Ca²⁺, which was particularly prone to deposition, decreased by 10.41%, and that of Mg²⁺ decreased by 2.88%. ICP analysis of the acid solution after immersion (Figure 6d) showed a significant amount of Mg²⁺, indicating effective removal of the ions responsible for degradation by dissolution in nitric acid. Therefore, we hypothesize that the voltage reduction after acid treatment was due to the removal of metal ions from the MEA by nitric acid, thereby reducing the amount of impurities. However, the amount of Ca²⁺ dissolved in nitric acid was very low, which may explain why voltage recovery was incomplete immediately after the treatment. The gradual voltage decrease at later times was thought to be a combined effect of acid treatment and subsequent flushing with ultrapure water. Another possible recovery mechanism is that metal ions bound to the sulfonic acid groups of the MEA were replaced by protons (H⁺) from dissociated nitric

acid, thereby restoring the MEA to its initial state. This principle has also been utilized for the regeneration of other cation-exchange resins possessing sulfonic acid groups, which is a situation similar to that of Nafion membranes [57–59]. Note that EDX analysis only provides information at the observed cross-section and does not represent the entire membrane. Therefore, the EDX results were used qualitatively to support the recovery mechanism, rather than as quantitative evidence of total metal removal.

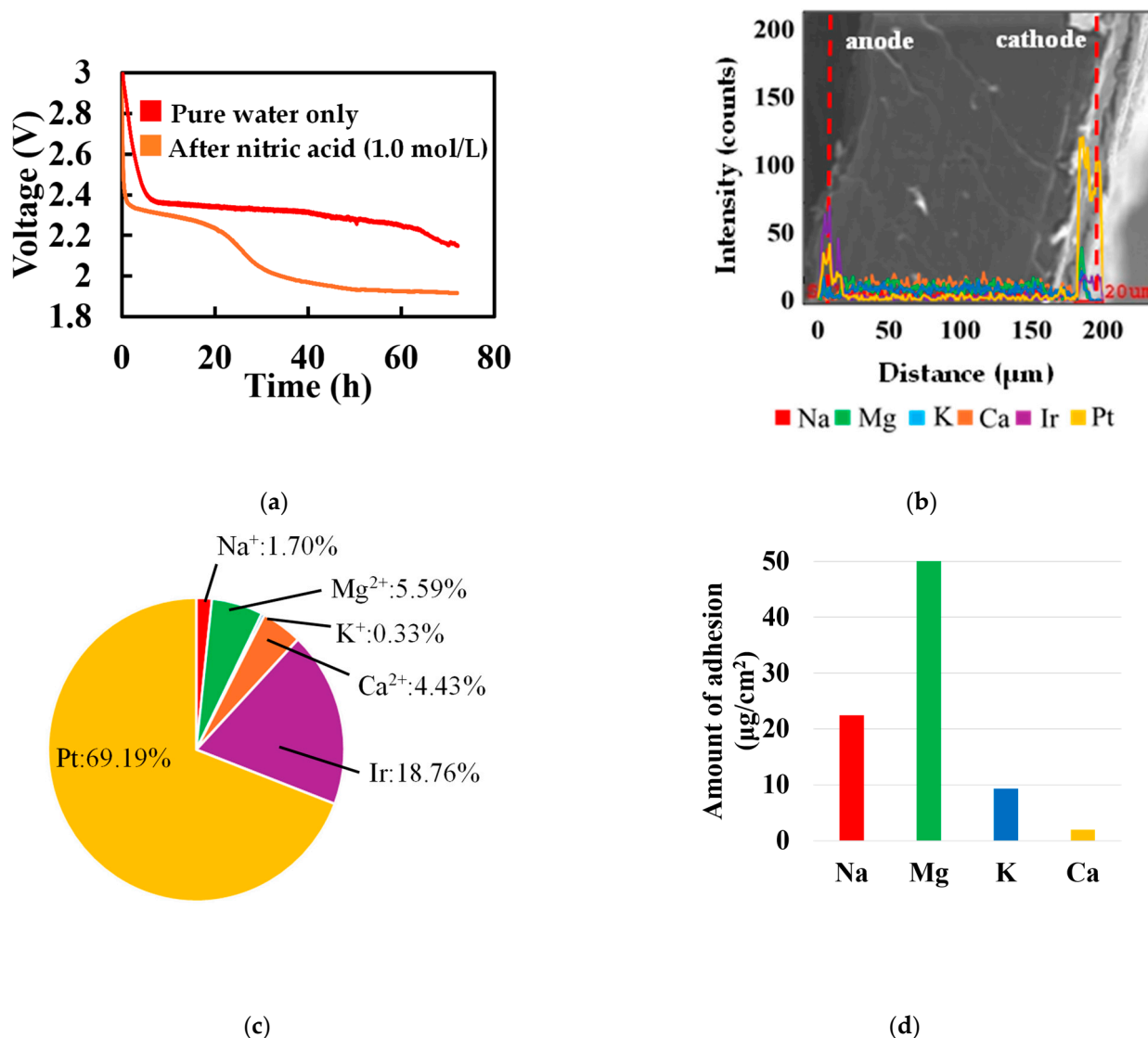


Figure 6. Recovery behavior after 24-h in-situ treatment with 1.0 mol/L nitric acid. (a) Representative cell-voltage profile during the subsequent 72-h operation with ultrapure water, compared with recovery using ultrapure water alone without acid treatment. (b) Representative cross-sectional SEM image of the recovered MEA. (c) Local elemental composition obtained by SEM-EDX. (d) Concentrations of contaminant ions detected by ICP in the collected nitric acid solution after treatment.

Calcium nitrate is highly soluble in water; however, nitrate ions only form weak outer-sphere complexes with Ca^{2+} [60,61]. Therefore, even when Ca^{2+} is released from the sulfonic acid groups of the membrane, it may re-associate with the fixed anionic sites on the membrane instead of remaining in the bulk solution. This is consistent with the low Ca^{2+} concentration observed in the ICP analysis of the nitric acid solution after immersion. The reduction in operating voltage was attributed to the restoration of proton conductivity in the membrane. Metal ions such as Ca^{2+} and Mg^{2+} replace protons in the sulfonic acid

groups, decreasing the number of available proton-conducting sites. Therefore, the removal of these ions through acid treatment directly contributes to the recovery of membrane conductivity, and consequently, to the reduction in cell voltage.

3.3. Results of Phosphoric Acid Immersion

Figure 7 shows a comparison of the voltage profiles following three recovery treatments: ultrapure water only without immersion in acid (from the previous study) and ultrapure water after immersion in concentrated (12.9 mol/L) and dilute (1.0 mol/L) phosphoric acid in the current study. Compared with the case without acid treatment, phosphoric acid immersion, particularly in the concentrated solution, resulted in better voltage recovery. For 12.9 mol/L phosphoric acid, the voltage recovery ratio increased from $95.2 \pm 3.6\%$ (mean $\pm$ SD, $n = 3$) at the beginning of the operation to $97.1 \pm 2.2\%$ (mean $\pm$ SD, $n = 3$) after 24 h and finally reached $99.1 \pm 1.5\%$ (mean $\pm$ SD, $n = 3$) after 72 h. In comparison, the voltage recovery ratio without acid immersion was $81.0 \pm 1.1\%$ (mean $\pm$ SD, $n = 2$) after 24 h and $89.2 \pm 3.3\%$ (mean $\pm$ SD, $n = 2$) after 72 h. For 1.0 mol/L phosphoric acid, the voltage recovery ratio was 86.0% after 12 h, 86.8% after 24 h, and 89.2% after 72 h ($n = 1$ in these cases). Note that immersion in 1.0 mol/L phosphoric acid did not change the voltage recovery ratio compared with the case without acid immersion. The recovery ratio of the hydrogen generation rate after 72 h was $101.2 \pm 1.0\%$ (mean $\pm$ SD, $n = 3$) for 12.9 mol/L phosphoric acid and 98.1% ($n = 1$) for 1.0 mol/L phosphoric acid. Again, the latter value is comparable to the case without acid immersion ($98.1 \pm 4.4\%$, mean $\pm$ SD, $n = 2$). These results indicate that phosphoric acid immersion improved voltage recovery while maintaining the hydrogen generation performance.

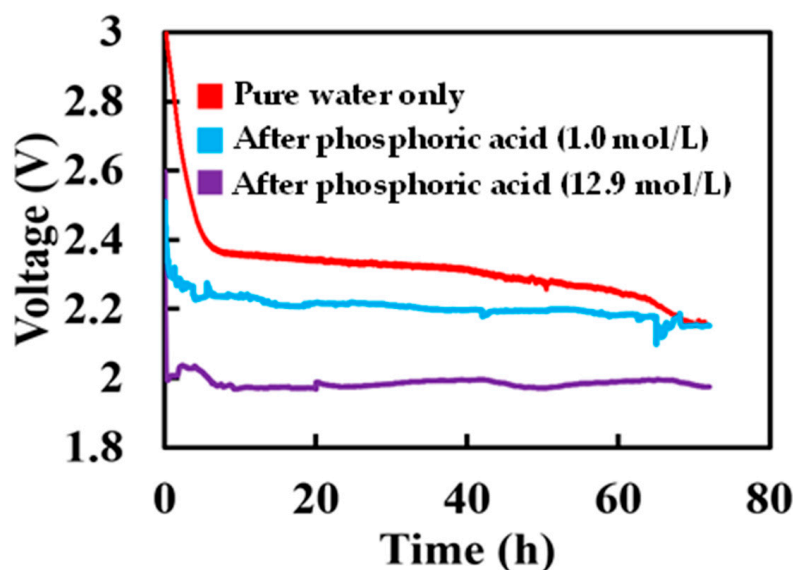


Figure 7. Comparison of voltage profiles for degraded MEAs treated with phosphoric acid (blue: 1.0 mol/L, purple: 12.9 mol/L) and without acid treatment (red).

Furthermore, Figure 8a,b and Figure 9a,b present SEM-EDX analyses of the MEA cross-sections after immersion in phosphoric acid at the two concentrations. In both cases, there was a significant reduction in the deposition of Mg^{2+} and Ca^{2+} , which were the main contaminants, compared with the state after degradation with artificial river water (Section 3.1). In the EDX analysis, only one part of the membrane cross-section was observed. Therefore, the obtained data may vary slightly depending on the observation location and only provide a qualitative explanation of the voltage recovery. Additionally, Figures 8c and 9c present the ICP analysis results of the phosphoric acid solutions after

immersion, confirming the dissolution of contaminant metal ions during acid treatment. Although the absolute concentrations varied among the experiments, Ca^{2+} and Mg^{2+} were detected, indicating the removal of these ions from the membrane. However, Ca^{2+} ions were not detected in the 1.0 mol/L phosphoric acid (Figure 9c), whereas all four metal ions were detected in the 12.9 mol/L phosphoric acid (Figure 8c). Except for this case, Mg^{2+} and Ca^{2+} (the ions with the most significant impact on degradation) were found in abundant amounts in the phosphoric acid solutions after immersion.

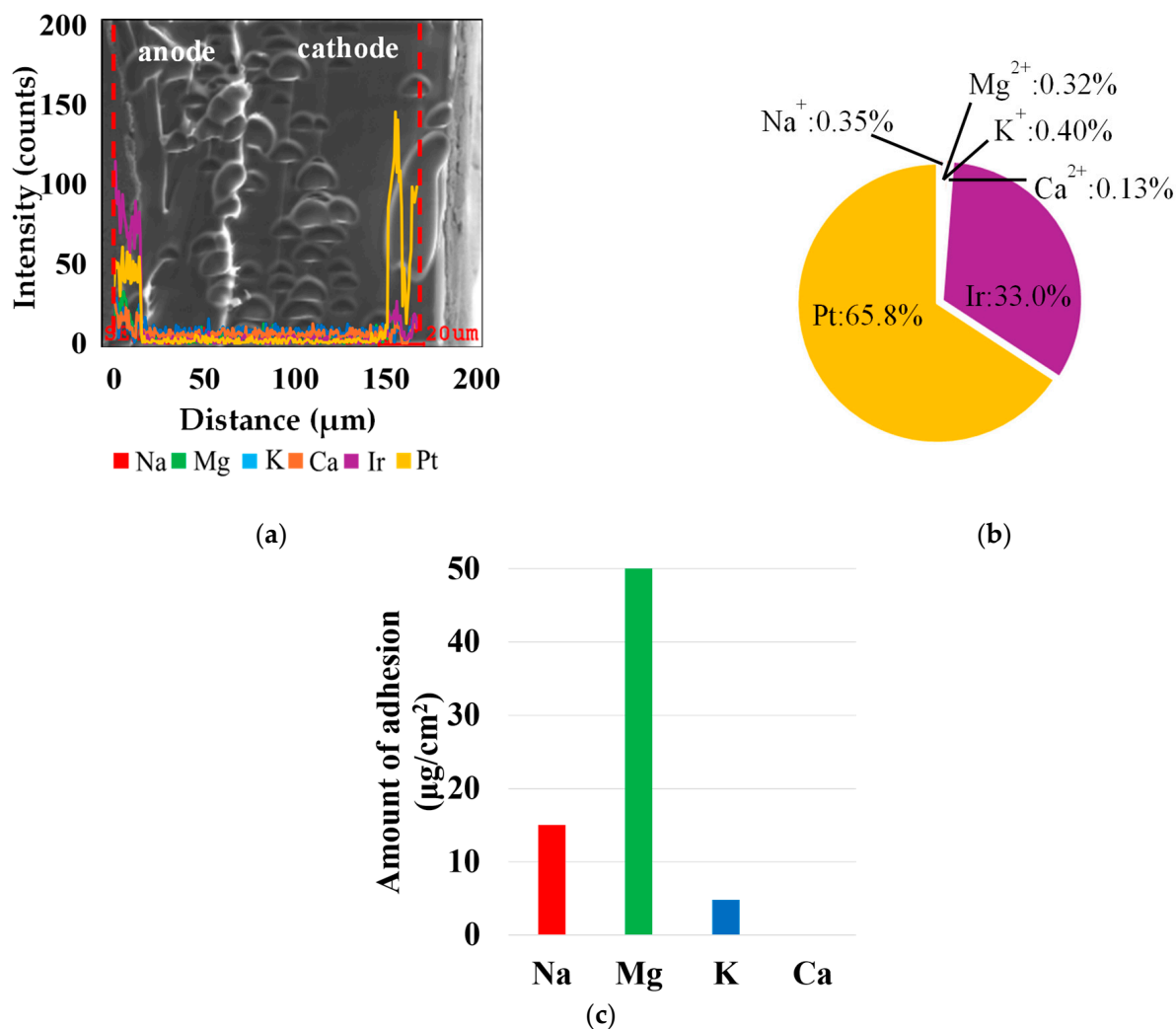


Figure 8. (a) Cross-section of the MEA after immersion in 1.0 mol/L phosphoric acid. (b) Weight percentage of metal ion deposits measured on a cross-section. (c) Ion concentrations in the 1.0 mol/L phosphoric acid after immersion treatment, measured by ICP.

Unlike nitric acid, phosphoric acid provides phosphate species that interact strongly with Ca^{2+} and Mg^{2+} , forming calcium and magnesium phosphate precipitates. Because these precipitates are thermodynamically stable and do not re-dissolve, the metal ions are effectively removed from the membrane [62–64]. This explains the sharp voltage drop observed immediately after immersion in 12.9 mol/L phosphoric acid.

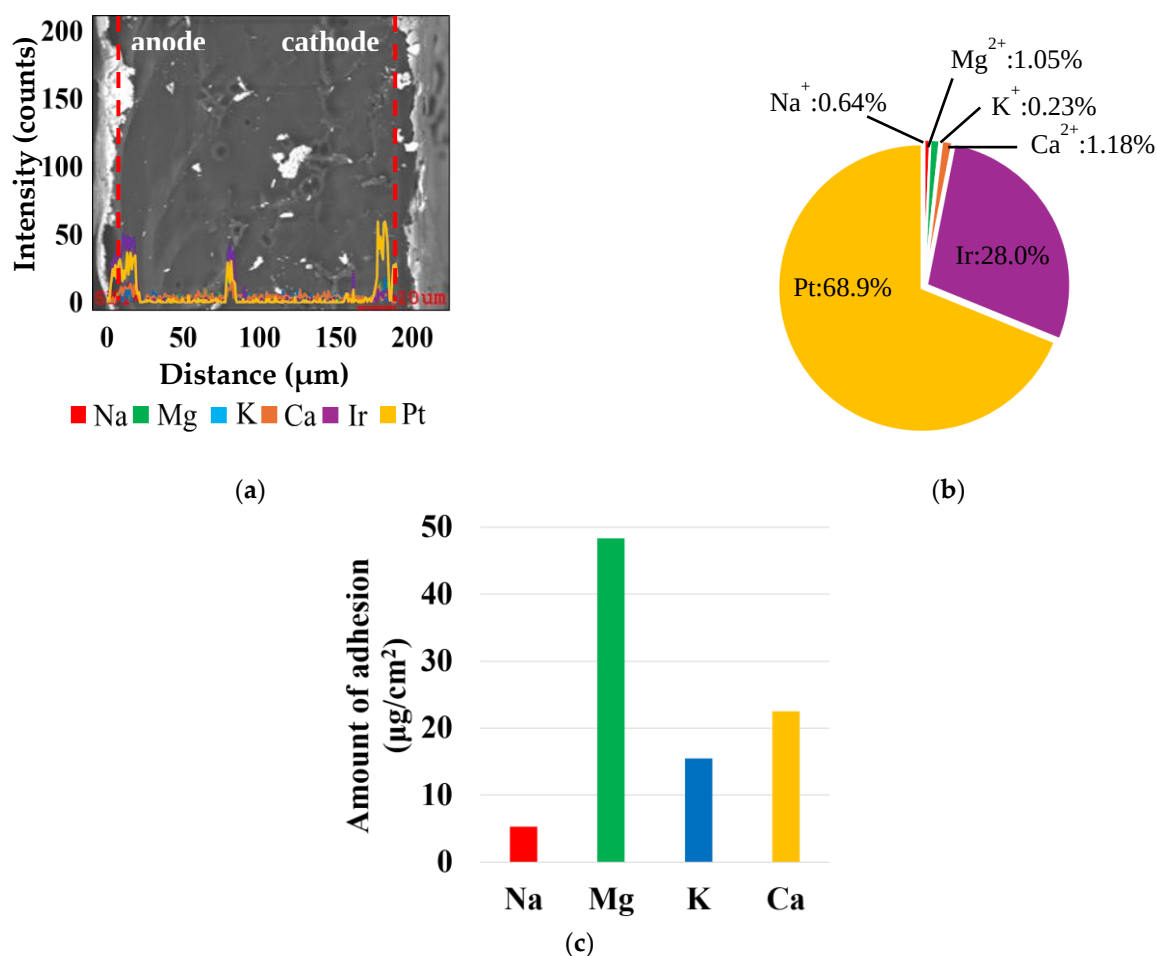


Figure 9. (a) Cross-section of the MEA after immersion in 12.9 mol/L phosphoric acid. (b) Weight percentage of metal ion deposits measured on a cross-section. (c) Ion concentrations in the 12.9 mol/L phosphoric acid after immersion treatment, measured by ICP.

4. Discussion

Based on the findings in Section 3.2, we hypothesize that cell recovery involves restoring the MEA to its initial state via ion exchange between metal ions bound to the sulfonic acid groups and protons generated by acid dissociation. This implies that the hydrogen ion concentration in the acid used for immersion is an important factor in cell recovery. Therefore, we calculated the proton concentration, $[H^+]$, in the three acid solutions from the corresponding acid dissociation constant K_a [65].

$$[H^+] \simeq \sqrt{cK_a}$$

where c denotes the acid concentration. Using this relation, $[H^+]$ for the phosphoric acid solutions was estimated from the first dissociation equilibrium constant ($pK_a = 2.16$ or $K_a = 6.9 \times 10^{-3}$). Note that this estimation does not consider ionic activity, which can become important in highly concentrated acid solutions. The obtained $[H^+]$ values are 3.0×10^{-1} mol/L at 12.9 mol/L and 8.3×10^{-2} at 1.0 mol/L. In ultrapure water, $[H^+]$ is 1.0×10^{-7} mol/L.

Figure 10 plots the average voltage recovery ratio (relative to the pre-degradation voltage) at 1 h post-immersion against the calculated $[H^+]$ of the phosphoric acid solution. The voltage recovery ratio generally increases with increasing $[H^+]$. Nevertheless, the recovery behavior cannot be explained by the proton concentration alone. In addition to proton availability, interactions between acid anions and dissolved metal ions should also

be considered. Phosphate species can interact with Ca^{2+} and Mg^{2+} through precipitation and/or complex formation, which may prevent the re-deposition of these contaminant ions onto the sulfonic acid groups of the membrane. Therefore, the recovery process is likely governed by both proton-driven ion exchange and the ability of acid anions to immobilize the dissolved metal ions. In particular, 1.0 mol/L nitric acid as described in Figure 6, which provides the highest $[\text{H}^+]$, did not exhibit the fastest recovery, indicating that additional chemical interactions influence the recovery process.

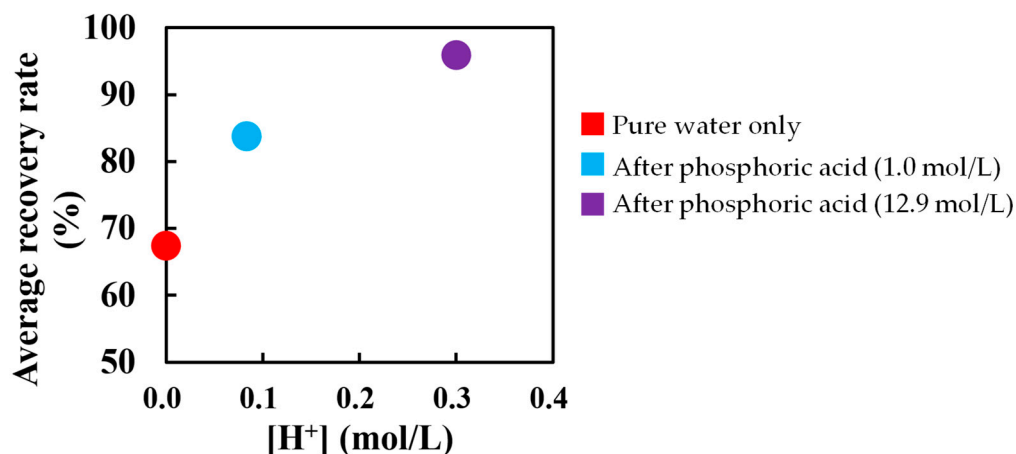


Figure 10. Relationship between the average voltage recovery ratio (voltage at 1 h post-immersion versus initial voltage before degradation) and proton concentration.

To further investigate this behavior, we examined the ICP results for the acids after MEA immersion. As described in Section 3.2, Ca^{2+} and Mg^{2+} were the primary contaminant ions responsible for cell degradation. The significantly higher Ca^{2+} concentration detected in 12.9 mol/L phosphoric acid compared with 1.0 mol/L nitric acid indicates that phosphoric acid removed more Ca^{2+} from the membrane during recovery, which is consistent with the rapid voltage decrease observed after immersion. This difference is likely associated with the characteristics of the acid anions. Compared with NO_3^- , phosphate species can immobilize released Ca^{2+} by forming sparingly soluble calcium phosphate and phosphate–metal complexes [63,66,67], thereby suppressing the redeposition of dissolved Ca^{2+} onto the sulfonic acid groups of the membrane. In contrast, NO_3^- has only a limited ability to stabilize dissolved metal ions under the conditions employed in this study, which may contribute to the slower recovery observed with nitric acid. Although 1.0 mol/L phosphoric acid contained the same phosphate species, its lower proton and phosphate concentrations resulted in a less pronounced recovery than that achieved with 12.9 mol/L phosphoric acid. Overall, these findings indicate that the recovery behavior of the MEA is governed by the combined effects of proton-assisted ion exchange and phosphate-mediated stabilization of released contaminant ions, rather than by the proton concentration alone.

The immersion time in this study was set to 24 h to enable rapid recovery within shorter durations, which is critical for reducing maintenance costs and realizing future industrial deployment. Considering safety and cost-effectiveness, it would be advantageous to use a lower phosphoric acid concentration than 12.9 mol/L to achieve equivalent recovery performance. Therefore, strategic optimization of the immersion time and phosphoric acid concentration is imperative for future research. Furthermore, although the proposed recovery mechanism was supported by electrochemical performance, SEM-EDX, and ICP analyses, electrochemical impedance spectroscopy (EIS) was not performed in the present study even though it provides valuable quantitative information on changes in

membrane resistance during the recovery process. Therefore, future studies should include EIS measurements to further verify the proposed recovery mechanism.

We note several practical limitations of the proposed recovery method. The long-term durability of the recovered cells and the effects of repeated acid treatments on the PEM components have not been fully evaluated. Additional studies are required to investigate the possible degradation of the membrane and catalyst layers during repeated treatments. While this study was conducted using a laboratory-scale cell, future research should evaluate the method's applicability to industrial-scale systems, including treatment uniformity, chemical recovery, and compatibility with stack configurations.

5. Conclusions

PEM water electrolysis converts surplus electricity into hydrogen, but it requires costly ultrapure water for long-term operation and precious-metal catalysts in the MEA. This study aimed to identify promising acid treatments to restore cell performance after operating with artificial river water containing various metal ions. Specifically, we investigated in-situ chemical recovery without disassembling the MEA as a simpler and less invasive procedure.

Operation with artificial river water led to an increase in the cell voltage, reaching the recommended replacement threshold of 3.0 V in approximately 6.6 h, accompanied by a decrease in hydrogen generation. SEM-EDX results further confirmed the deposition of cations on the membrane, which increased the membrane resistance and operating voltage, leading to performance degradation. We then tested three acid solutions for immersing the MEA: 1.0 mol/L nitric acid (used in a previous study, albeit with cell disassembly), 12.9 mol/L phosphoric acid (a weaker and safer acid), and 1.0 mol/L phosphoric acid. We also compared the results with those of a previous study that directly operated the degraded cell with ultrapure water and no immersion treatment. Based on the SEM-EDX and ICP results, 12.9 mol/L phosphoric acid was found to be the most effective. Similar to the case of cation-exchange resins, cell voltage recovery in this study was also positively correlated with proton concentration in the acid solution, suggesting that higher proton concentrations can accelerate restoration of the membrane to its initial state. Meanwhile, the anions in the acid also played a role because phosphate species were better at preventing dissolved metal ions (especially Ca^{2+} and Mg^{2+}) from re-depositing on the membrane. Therefore, the recovery performance was jointly determined by the proton concentration in the acid and the chemical affinity between acid anions and deposited metal ions. Future work should focus on identifying the optimal immersion time to accelerate recovery.

Overall, this study developed a novel in-situ recovery method for degraded PEM water electrolysis cells without cell disassembly, providing a practical strategy for extending cell lifetime while simplifying the recovery process.

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Abbreviations

The following abbreviations are used in this manuscript:

PEM	Polymer Electrolyte Membrane
MEA	Membrane Electrode Assembly
SEM	Scanning Electron Microscopy
EDX	Energy-Dispersive X-ray Spectroscopy
ICP	Inductively Coupled Plasma

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