

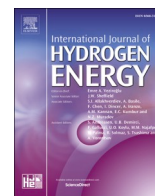


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Performance recovery of proton exchange membrane electrolyzer degraded by metal cations contamination

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ABSTRACT

Hydrogen production from renewable electricity offers an eco-friendly alternative to fossil fuels. Proton exchange membrane (PEM) electrolysis is a well-known method for this purpose. Studies have primarily focused on reducing costs of noble catalysts, improving efficiency, managing system degradation, and addressing membrane thinning caused by contaminated cations. However, techniques for PEM recovery post-degradation are still under development. This study investigated the effects of cations on PEM cells using artificial soft water, and analyzed two recovery methods to restore cell performance. Our findings indicate a significant rise in cell operating voltage and a decrease hydrogen production over 8 h of operation with soft water. After introducing both recovery methods, the initial operating value was reinstated in both cases. Only nitric acid treatment, however, achieved hydrogen production levels comparable to those of ultrapure water.

1. Introduction

Renewable energy, such as solar and wind power, holds promise as a clean energy source to address global environmental issues. However, ensuring a stable power supply is challenging due to their fluctuating production under varying climate conditions, resulting in uneven regional distribution. Hydrogen production through water electrolysis using a surplus renewable electricity has garnered attention as a viable alternative. This process yields carbon-free hydrogen, offering a higher energy density than other solid fuels [1–3].

Various electrolysis processes are being developed to extract hydrogen from renewable sources. Among them, PEM electrolysis is renowned for its high efficiency (80–90 %) and high hydrogen purity (99.99 %), and oxygen as byproducts. They can operate at lower temperatures (20–80 °C) and high current densities (over 2 Acm⁻²) [1, 3–14]. However, it faces barriers such as high capital cost and PEM membrane degradation issues arising from contaminated cations. The presence of cationic contaminants can significantly reduce fuel cell performance because these impurities can enter the MEA directly, poisoning catalyst sites, blocking proton transport, and inhibiting oxygen transport. This can result in a variety of performance losses, such as ohmic loss, mass transport loss, and kinetic losses at the anode and

cathode [15]. Researchers have investigated the degradation matters due to contaminated cations [16–29] and provided low-cost metal catalysts [10,30–35]. Extensive research has been conducted to determine the effect of cationic impurities such as iron (Fe³⁺) and copper (Cu²⁺) on membrane conductivity, cell electrode durability for both PEM fuel cells and water electrolyzers, as well as to model the effects of cationic contamination on PEM cell performance [37]. Common impurities in the feed water of PEM-type electrolysis include iron (Fe³⁺), magnesium (Mg²⁺), calcium (Ca²⁺), copper (Cu²⁺), and sodium (Na⁺) cations [17, 20,36–49].

The American Society for Testing and Materials (ASTM) recommends Type I deionized water – water containing less than 50 ppb of total organic carbon, a resistivity of more than 1 MΩ-cm, and less than 5 μg/L of sodium and chloride content – for commercial PEM electrolyzers [52]. However, almost all water resources are not pure, and water treatment involving several filtration steps adds to the capital cost of the PEM electrolysis, as it requires pure water. Due to the high cost of purification, as well as the scarcity of groundwater or potable water in many areas, there is growing academic interest in developing electrolyzers that can operate on lower quality water [54]. As the membrane electrode assembly (MEA) serves as a cornerstone of PEM, the migration of cations from the feed water results in cell degradation. The membrane of

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a PEM cell separates hydrogen and oxygen into the anode and cathode, which are both attached to the membrane. Protons (H^+ ions) are transferred to the cathode during the electrolysis. Accumulated cations at the electrodes increase ohmic losses and replace H^+ ions, raising cell voltage and MEA conductivity [17,20,47–49]. Therefore, providing cation-free pure water is crucial for PEM water electrolysis. Purification methods involve using ion exchange resin or reverse osmosis (RO) membrane filtration on river water [50,51]. If applied to large-scale renewable-based hydrogen production, it would require substantial water sources and inflate the overall costs. More recently, techniques have been developed to remove ions and desalinate seawater [53–57]. These techniques, which are critical in preventing cation-induced degradation, highlight the importance of water purity and the potential for these methodologies to evolve into more effective cation management solutions.

The cost of water treatment for electrolysis is expected to decrease with easily accessible artificial water requiring minimum purification. However, artificial water may contain unknown cations, necessitating an assessment of their effects on PEM processes. Water contaminants influenced the cell voltage of the PEM electrolyzer, resulting in a higher cell voltage than with pure water. Because the efficiency of the electrolyzer is inversely proportional to its resultant voltage, the presence of higher concentrations of cationic elements reduced the cell's efficiency. As a result of the increased cell voltage caused by water contaminants, energy efficiency and energy consumption in the electrolyzer decreased [58]. Several reports have focused on single-cation contaminations from feed water [36–47] and explored ways to optimize PEM efficiency [59–65]. However, no comprehensive reviews have assessed PEM-electrolysis performance using artificial water with mixed cations. Additionally, the effect of cations that should be intensively excluded from artificial water has not been reviewed.

In our previous study, we introduced artificial soft water to the PEM electrolyzer and analyzed the cations attached to the PEM cell [66]. The impurities found in this type of soft water included Ca^{2+} , Mg^{2+} , Na^+ , and potassium (K^+), common impurities in river water. We also detailed how these cations affected PEM performance in terms of cell voltage and hydrogen-production rate. Using SEM image, the distribution of the contamination was evaluated. Cell voltage rapidly increased with the increasing amounts of divalent cations (Ca^{2+} and Mg^{2+}) adhered to the PEM membrane. As a result, the presence of cation elements reduced the conductivity of the membrane electrode assembly (MEA), and PEM cell performance was affected due to the replaced cations [66].

Although extensive research has been conducted on the impact of cationic impurities on membrane properties and fuel cell performance, analyzing methods to recover the performance of electrolysis cells remains a challenging task. Therefore, in this study, we analyzed the two methods to recover voltage and maintain hydrogen generation after PEM cell degradation. After recovery treatment, the results were compared to identify an effective recovery method that restores PEM performance after severe degradation.

2. Materials and methods

2.1. PEM single-cell assembly

This study used a water electrolyzer (EHC 070) manufactured by Enoah Int. Fig. 1 shows the cell structure of the PEM electrolyzer, featuring porous feeders and multi-pole plates situated at both ends of the MEA, with an effective MEA of 11.34 cm^2 . A catalytic electrode is affixed to the surface of the electrolyte membrane. As the cathode catalyst, platinum (Pt) is employed. Pt group metals have exceptional catalytic properties due to their strong acidity and alkalinity and superior heat endurance. The anode catalyst in this instance is an iridium (Ir) catalyst. Because of its strong catalytic properties against the oxidation reaction of water, it is employed as an electrode in the production of oxygen [35]. We conducted experiments under a constant current of 9 A,

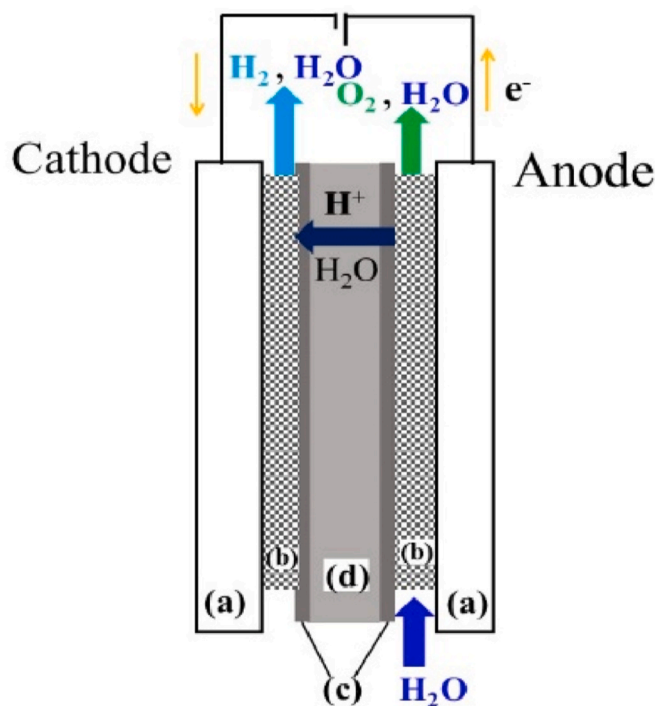


Fig. 1. Configuration of a PEM water electrolysis cell which includes (a) compound electrode plates, (b) porous feeders, (c) catalyst electrodes, and (d) proton exchange membrane.

not exceeding a maximum allowable current of 10 A, while maintaining the operational cell voltage between 1.8 and 2.3 V. This was critical for avoiding performance degradation, which occurs when the cell voltage exceeds the 3 V threshold.

2.2. Preparation of soft water and experimental setup

River water was used as soft water and artificially prepared by adding salt to ultrapure water, as shown in Table 1. The methodology and detailed compositions for producing soft water have been published by the American Public Health Association (APHA) [48]. We investigated the effects of cations (Na^+ , Mg^{2+} , K^+ , and Ca^{2+}) adhered to the cell before and after soft-water supply. Fig. 2 provides a schematic illustration of the experimental setup. We supplied soft water from the bottom part of the cell with a flow rate of 1.5 mL/min . The cell was operated at a current density of 0.79 Acm^{-2} (9.0 A). Hydrogen was generated at the cathode with byproduct water. Oxygen and unreacted water were discharged at the anode port. After passing through a gas-liquid separator, the generated gas was dried through molecular sieves. The hydrogen generation rate was measured using a mass flow meter. The operating current of the PEM cell was calculated by a shunt resistor ($1\text{ m}\Omega$) inserted into the circuit. We measured the operating cell voltage (V_{cell}), the voltage between the shunts (V_R), and the hydrogen generation rates (r_H), during the experimental period. These experiments were performed at

Table 1
Summary of the composition of artificial soft water.

Water type	Soft water	
Salts Required (mg/L)	$NaHCO_3$	48
	$CaSO_4 \cdot 2H_2O$	30
	$MgSO_4$	30
	KCl	2.0
Water Quality	pH	7.2–7.6
	Hardness (mg/L)	40–48
	Alkalinity (mg/L)	30–35

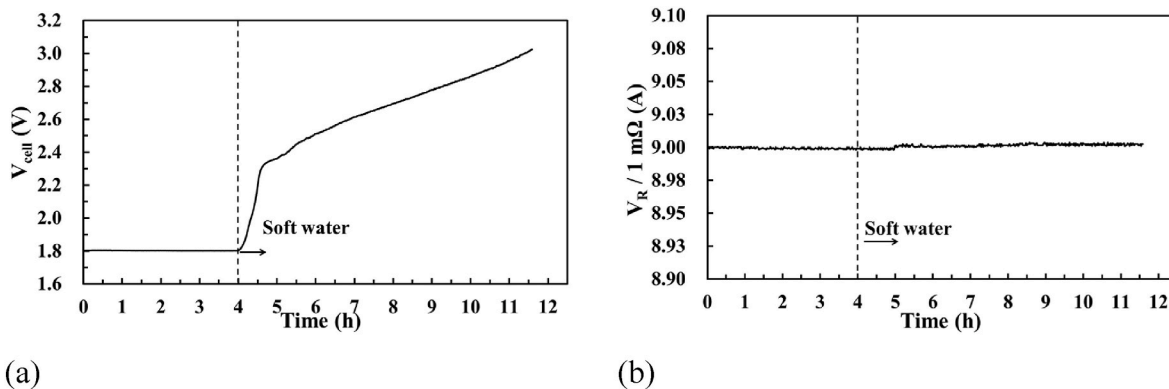


Fig. 3. Test results of artificial soft water electrolysis (a) operating voltage, (b) operating current.

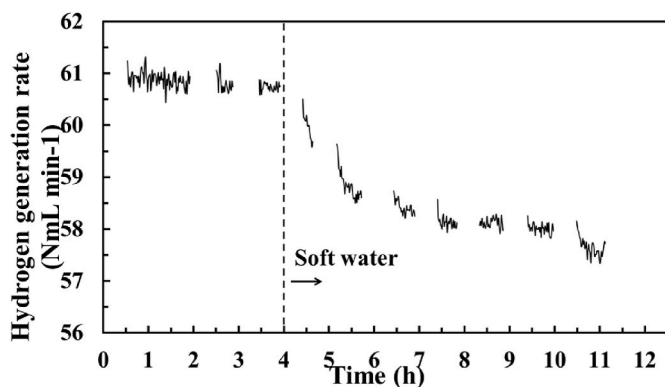


Fig. 4. Hydrogen production rate profile during soft water analysis.

process, the voltage rapidly decreased at a rate of 0.092 V h^{-1} within the first 8 h. After that, it gradually decreased with a rate of 0.004 V h^{-1} until the voltage reached below 1.81 V (the initial operating voltage). This suggests that the transition process from



to



occurred at the cathode during the early stages of pure water recovery. This process was dominated by Na^+ contaminants, which increased the cell voltage during the artificial soft water electrolysis. This can be attributed to two main reasons. Firstly, cations replaced H^+ ions, leading to an insufficient number of protons to perform the primary

reaction, as shown in Equation (2). Accordingly, Equation (3) took effect instead. Secondly, a reduction in the electrical conductivity of MEA occurred due to the presence of adhered cations [38]. Consequently, during the ultrapure water recovery process, there was a sufficient supply of protons as cations were fully discharged. The results indicate that the recovery process decreased the increasing voltage because the reaction gradually shifted back to the original cathode reaction, with the electric field mobilizing the ions. H_3O^+ and water replaced metal hydroxides, further contributing to the reduction in voltage.

Conversely, the hydrogen generation rate did not increase during the ultrapure water recovery treatment and continued to decline, as shown in Fig. 7 (b). While the voltage was declining, the hydrogen generation rates remained stable at approximately 45 N mL/min for 95 h. Afterward, it decreased again. This indicates that the removal of cations by ultrapure treatment does not fully restore the structure of the electrolyte

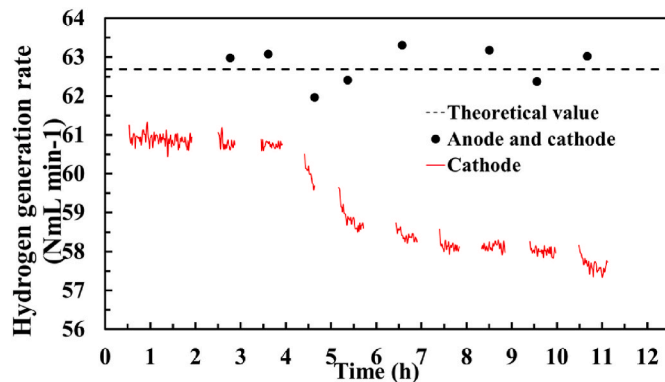


Fig. 6. Total hydrogen generation rate (from cathodes and anode) by the cell.

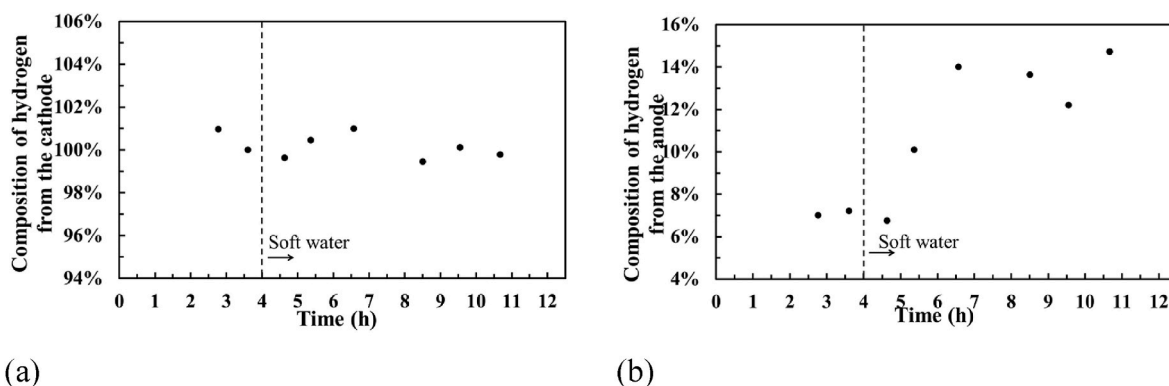


Fig. 5. Composition of hydrogen on (a) the cathode and (b) the anode.

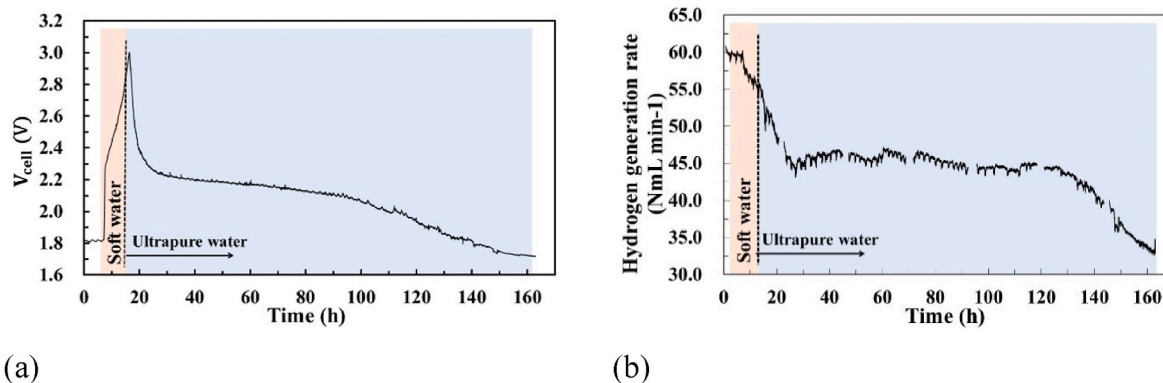


Fig. 7. Analysis of (a) operating voltage and (b) hydrogen generation rate during recovery treatment with ultrapure water.

membrane and hydrogen generation.

3.3. Immersing contaminated MEA into the nitric acid

As an alternative method to recover cell performance, we used nitric acid to remove the cations adhered to the MEA. After the soft water electrolysis, the contaminated MEA was inserted into the nitric acid for approximately 20 h. Then, ultrapure water was supplied to the system. The results were measured and analyzed during the operation period. Fig. 8 (a) and (b) show the measured results of operating voltage and hydrogen production rate after the nitric acid treatment.

As provided in Fig. 8 (a) and (b), the performance of the cell was recovered in both voltage and hydrogen generation. After the nitric acid treatment, the operation was performed for approximately 50 h, maintaining a stable voltage and hydrogen generation. The replacement of cations by the sulfonic acid groups and the removal of metal hydroxides are the main factors that decrease the voltage during the artificial soft water electrolysis [42,43]. However, both voltage and hydrogen generation were restored after nitric acid treatment. This suggests that the H⁺ ions replaced the cations and reattained the molecular structure of the electrolyte membrane after treatment with nitric acid, resulting in reduced gas permeation.

In this study, we discussed the two methods for recovering the performance of PEM cells after degradation by cation contamination. Comparing the aforementioned methods, the increasing cell voltage was reduced and recovered in both cases. However, the decrease occurred gradually and required time during ultrapure water electrolysis treatment. Conversely, the effect on the hydrogen generation rate was only observed after nitric acid treatment. Therefore, the recovery method involving nitric acid treatment has the potential to restore the PEM cells that have been degraded by artificial soft water electrolysis. To support this claim, we measured the concentration of adhered cations in the

MEA during the soft water electrolysis and treatment methods using ICP emission analysis. Fig. 9 depicts the amount of attached cations during the experimental period.

As shown in Fig. 9, the concentrations of cations were measured before soft water electrolysis (1.85V), after the cell was affected by cations contamination (3.00V), and after each recovery treatment. Both the amount of divalent (Mg²⁺, Ca²⁺) and monovalent (Na⁺, K⁺) cations were significant during soft water electrolysis. After cell recovery using both methods, cation adhesion levels were approximately similar to those before contamination. Therefore, it was verified that the two recovery treatments removed cations that adhered to the MEA, whereas nitric acid treatment suppressed the structure of the membrane and amount of gas permeation. This study suggests that nitric acid treatment is an efficient method for removing cationic contaminants due to

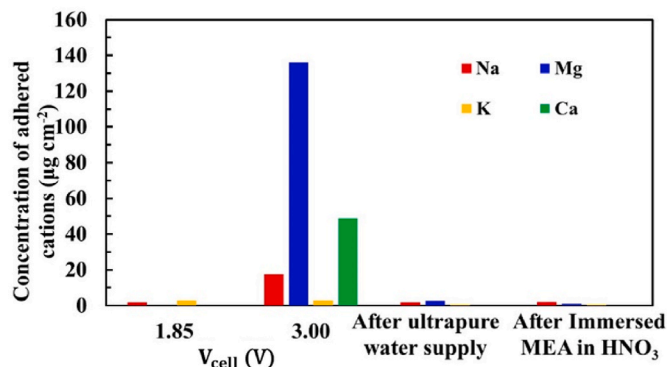


Fig. 9. Comparison of concentration of cations before soft water electrolysis, during contamination period, and after recovery with ultrapure water electrolysis and nitric acid treatment.

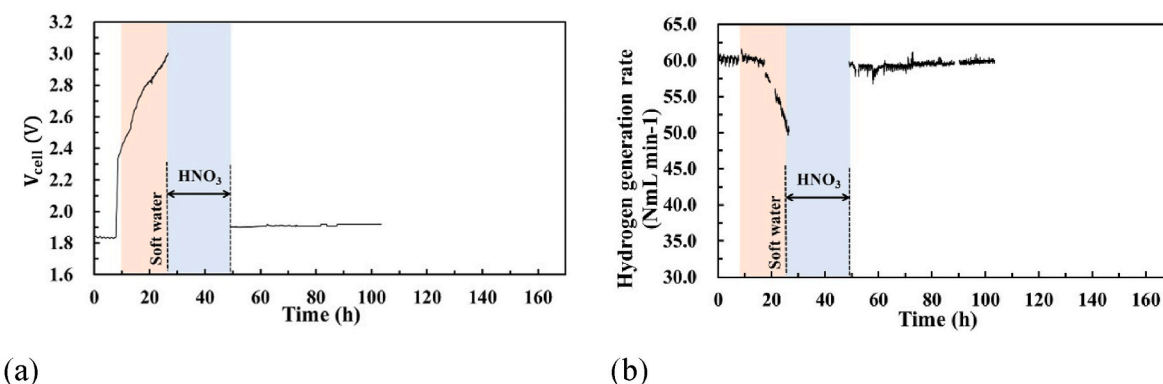


Fig. 8. Test results analysis after recovery process with nitric acid (a) operating voltage and (b) hydrogen generation rate.

impurities in artificial soft water and recovering the voltage and hydrogen production rate of PEM cells.

4. Conclusions

Cation contamination of the MEA poses a significant risk to PEM performance and the structural integrity of water electrolysis. Since the structure of MEA is affected by cation movement, there is an increasing possibility of hydrogen permeation through the membrane. We used artificial soft water to reduce the capital cost of PEM-type electrolysis and investigated the effects of cations initiated by it. The main cations (Na^+ , Mg^{2+} , K^+ , and Ca^{2+}) significantly increased the voltage and affected cell performance. We also found that cation contamination deteriorated cell structure and resulted in hydrogen-gas permeation through the membrane.

In this study, we presented recovery methods aimed at restoring PEM cell performance and examined voltage and hydrogen generation during the experiments. When ultrapure water was reintroduced after soft water electrolysis, the increasing cell voltage declined to the initial operating voltage (1.8 V). However, hydrogen generation decreased over the course of the operation. In contrast, nitric acid treatment was effective in both voltage and hydrogen-generation recovery, indicating an improvement in the degraded membrane structure. Comparing the two methods, the latter has the potential to restore degraded electrolyzer performance, with opportunities for further refinement by adjusting the operating conditions such as temperature and nitric acid concentration. However, the method needs to be disassembled and reconstructed of the electrolyzer. Developing cost-effective recovery methods that exhibit similar effects to the immersing nitric acid without reconstructing the electrolyzer is necessary in the future.

Author contributions

Conceptualization, Y.O. and K.N.; methodology, P.P.S.S., Y.S., and Y.O.; validation, P.P.S.S., S.W., and Y.O.; formal analysis, P.S.S.S., S.W., and Y.O.; data curation, S.W. and Y.O.; writing—original draft preparation, P.S.S.S., S.W.; writing—review and editing, P.S.S.S. and Y.O.; supervision, K.N.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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