Journal of Chemical Technology and Metallurgy, 60, 5, 2025, 823-831

ENHANCING REGENERATION SYSTEM CYCLIC STABILITY FOR ALL-IRON FLOW BATTERIES THROUGH NAFION MEMBRANE MODIFICATION WITH A SILICA NANOLAYER

Yaroslav Kolosovskyi, Oleksii Kosohin, Olga Linyucheva

National Technical University of Ukraine
"Igor Sikorsky Kyiv Polytechnic Institute"
37 Prospect Beresteiskyi St., Kyiv, 03056, Ukraine
yaroslav.kolosovskiy@yahoo.com (Y.K.); o.kosogin@kpi.ua (O.K.);
o.linyucheva@kpi.ua (O.L.)

Received 16 August 2024
Accepted 21 February 2025
DOI: 10.59957/jctm.v60.i5.2025.13

ABSTRACT

This study investigates the impact of modifying a Nafion N115 membrane with a silica nanolayer created from tetraethoxysilane (TEOS) on the performance and durability of an all-iron flow battery. The research aims to enhance electrolyte regeneration and reduce degradation issues commonly encountered in such systems. Potentiometric analysis and cyclic voltammetry were employed to assess the modified membranes' cyclic stability and electrochemical activity of the catalyst. The results demonstrate that the TEOS-modified membrane significantly improves cyclic stability, extending it to ten cycles, compared to just three cycles for unmodified membranes. Moreover, the modification effectively preserves the electrochemically active surface area of the platinum catalyst, thereby enhancing overall system performance and reducing catalyst degradation. The study concludes that the TEOS-modified Nafion membrane offers a viable solution to improve the durability and efficiency of all-iron flow batteries, making it a promising candidate for long-term energy storage applications.

Keywords: Nafion membrane, TEOS, all-iron flow battery, electrolyte regeneration, cyclic stability, catalyst degradation, energy storage, silica nanolayer.

INTRODUCTION

Ensuring sustainable development and energy supply is not just important, and it's critical in today's world. Population growth and increasing energy consumption drive governments and the scientific community to seek efficient and sustainable solutions for long-term energy storage.

One critical aspect of achieving these goals is the transition to renewable energy sources and the gradual abandonment of fossil fuels such as coal and oil. Solar and wind energy are becoming increasingly popular, but their production depends on natural conditions such as weather, leading to instability in energy generation. Therefore, ensuring long-term energy storage and efficient management becomes crucial for maintaining a continuous and reliable energy supply, underscoring the topic's significance [1].

Various energy storage technologies are being explored and developed to address these challenges. Vanadium redox flow batteries have gained wide recognition due to their potential to store large amounts of energy and provide a stable power supply during low generation from renewable sources. However, despite their advantages, such as high efficiency and low energy losses, they have limitations. The cost and limited reserves of vanadium pose obstacles to their widespread industrial application, underscoring the urgent need for further innovation in energy storage [2].

Among other energy storage technologies, lithium-ion battery systems are also widely used for storing energy from renewable sources. Distributed technologies such as physical springs and hydro accumulators can store large-scale energy for peak loads.

Despite the array of available technologies, efficiency, sustainability, and cost are crucial for achieving a sustainable energy supply. All-iron flow batteries stand out as an up-and-coming solution in this context. They offer a more economical and environmentally friendly option for long-term energy storage on an industrial scale and have the potential to revolutionize the energy storage landscape [3, 4].

The primary challenge with all-iron flow batteries lies in the regeneration of electrolytes, a problem that has garnered significant attention from the scientific community [5]. The main culprit behind electrolyte degradation is the side process of hydrogen evolution during charging, leading to an imbalance of electrolyte compositions and affecting flow batteries' current efficiency. While most scientific studies are focused on finding effective methods to minimize the amount of hydrogen formed through various additives, a complete solution to inhibit the side reaction of hydrogen evolution has yet to be developed. Furthermore, introducing additives to the electrolytes often increases the polarization of target reactions, thereby reducing the voltage efficiency of the battery [6 - 8].

Thus, the study of electrolyte regeneration in iron flow batteries becomes relevant to scientists. Finding optimal solutions can address issues related to electrolyte degradation, promoting the development of stable and efficient long-term energy storage systems on an industrial scale.

The studies showed the improvement of the hydrogen-iron system by modifying the proton-conducting membrane with a nanolayer of tetraethoxysilane (TEOS). This research focuses on optimizing the stability of the regenerative system. Comprehensive studies using potentiometric methods and cyclic voltammetry have been conducted to evaluate cyclic stability and electrochemical activity, respectively. The results provide compelling evidence for the effectiveness of the membrane modification approach.

The potentiometric analysis detected an increase in the cyclic stability of the rebalancing cell to more than three times that of the unmodified membrane, indicating a successful membrane modification that positively affects the system's stability. Additionally, studies reveal that the modified membrane reduces catalyst degradation compared to the unmodified one, confirming the modified membrane's ability to restrain catalyst degradation and enhance system stability.

This paper reviews the electrolyte regeneration systems in all-iron flow batteries and explores the possibility of developing optimal solutions for stable and efficient electrolyte recovery. We analyze the advantages and disadvantages of existing approaches and identify new opportunities for improving regeneration processes in flow batteries.

EXPERIMENTAL

Materials and equipment

The potentiometric studies were conducted using an IVIUM XP40 potentiostat. The cathode side of the regenerative cell utilized commercially available electrode material Sigracet 22 BB, with a layer of Pt/Vulcan catalyst with a loading of 0.2 mg cm^{-2} from The Fuel Cell Store (Bryan, USA). This electrode consists of carbon fibers treated with PTFE and contains a catalytic layer made of platinum catalyst on a carbon carrier on one side. The electrode thickness is 215 μm, with a 74.7 ± 10 % porosity.

The anode used was a pre-activated graphite felt (SGL Carbon) thermally treated at 450^{o}C for 2 h with a thickness of 3 mm. The electrodes' working area was 10 cm^{2}.

The proton-conducting membrane used as a separator in the working half-cells of the regenerative cell was Nafion® N115, with a thickness of 125 μm. Before use, the membrane was prepared according to this procedure: soaking for 60 min in a 3 wt. % H_2O_2 solution at 80^{o}C to remove possible organic contaminants, followed by 30 min in a 10 % H_2SO_4 solution at 80^{o}C for preliminary protonation. After treatment, the membrane was washed with deionized water to remove traces of H_2O_2 and H_2SO_4.

Membrane preparation method

The method for preparing the Nafion/SiO_2 hybrid membrane is based on the procedure outlined by Mauritz et al. [9].

An appropriate amount of Nafion solution was mixed with the calculated quantity of tetraethoxysilane (TEOS) in a magnetic stirrer. The mixture was continuously stirred to ensure proper distribution and interaction between the Nafion and TEOS components. The solution was then cast into a Petri dish and heated at 85°C for 15 h to remove the solvent. The recast membranes were detached from the Petri dish with the addition of bidistilled water. Excess water was removed using filter paper. The membranes were hot-pressed at 130°C and 60 bar for 3 min to improve mechanical strength. The prepared hybrid membranes were immersed in a 10 wt. % ammonia solution and stirred for 30 min at room temperature to obtain inorganic nanoparticles from the TEOS precursors. All membranes were sequentially treated with a 10 % solution of H_2O_2, a 5 % solution of HCl, and twice with bidistilled water at 80°C to ensure proper cleaning and activation of the membrane surface.

Experimental setup

The experimental setup consisted of a regenerative cell, a peristaltic pump for electrolyte delivery, and a PEM electrolyzer hydrogen source. The electrolytes used in the testing had the following composition: $FeCl_2$ (1.2 M), $FeCl_3$ (0.3 M), and NH_4Cl (2 M). The initial concentration of $FeCl_3$ was set at 0.3 M to simulate a 20 % state of charge of the positive electrolyte of the iron flow battery.

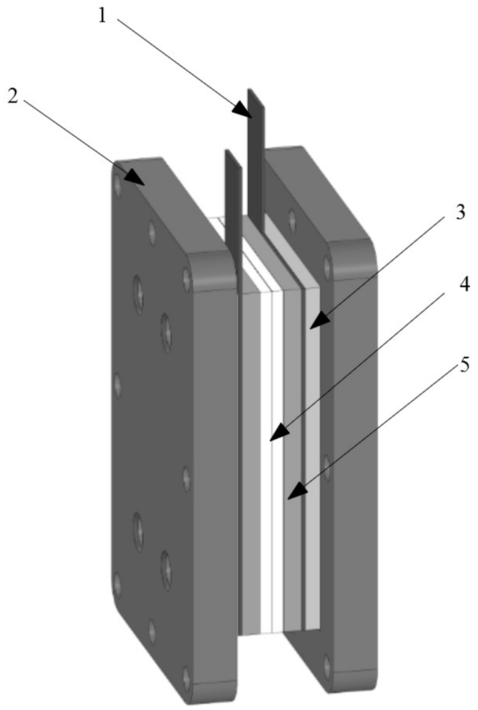

Fig. 1. Model of the regenerative cell used for cyclic stability testing of the modified membranes: 1 - copper current collector, 2 - sealing plate, 3 - insulating plate, 4 - membrane-electrode assembly, 5 - graphite electrode.

Cyclic stability assessment

The cyclic stability of the modified membranes was investigated using the regenerative cell developed in our study. This custom-designed cell was explicitly utilized to evaluate the performance and stability of the modified membranes under operating conditions.

The model of the regenerative cell used for these experiments is shown in Fig. 1. The cell was designed to simulate the working conditions of the membranes within the energy storage system, allowing for an accurate assessment of their durability and cyclic stability.

A series of experiments was conducted to regenerate a defined volume of electrolyte from 0.3 M $FeCl_3$ to 0.15 M $FeCl_3$, corresponding to the regeneration of 10 % of the electrolyte capacity. These experiments evaluated the cyclic stability of the regenerative cell.

A two-electrode setup was used for cyclic stability testing of the regenerative cell. In this configuration, the anode functioned as both the reference and counter electrode, allowing for the direct assessment of the membrane's performance under operating conditions.

Electrochemical studies

Electrochemical measurements were conducted using a standard three-electrode cell from Pine Research Instrumentation (Durham, USA) to evaluate the activity of the Pt catalysts. The working electrode was fabricated from a gas diffusion electrode with an area of 0.32 cm^{-2}, secured in a Teflon frame with a platinum current collector, which was externally insulated with Teflon. A platinum wire served as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. The potentials in the study are reported relative to the reversible hydrogen electrode (RHE). The voltages were converted to the RHE scale using the Nernst equation, with prior measurements of the pH values of the solutions used in the experiments.

The electrochemically active surface area (ECSA) was evaluated using the hydrogen adsorption charge method. Cyclic voltammetry (CV) was performed in a pre-deaerated background electrolyte (0.5 M H_2SO_4)

within a potential window of 0 to 1.4 V relative to RHE at a scan rate of 25 mV s^{-1} to determine the charge associated with hydrogen adsorption (H_ads). The ECSA was calculated based on the charge for hydrogen adsorption, assuming that the value required to form a monolayer of adsorbed hydrogen on Pt is 210 μC cm^{-2} [10].

SEM Microscopy and EDX Analysis

Scanning Electron Microscopy (SEM) was conducted at the National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute," using a Bruker SEM instrument. The modified membrane's surface morphology and elemental composition were analysed. The SEM analysis provided detailed images of the membrane surface, confirming the presence and uniform distribution of the silica nanolayer on the Nafion membrane. Energy-dispersive X-ray Spectroscopy (EDX) was also performed to determine the membrane surface's elemental composition**.**

RESULTS AND DISCUSSION

Microstructural analysis

The microstructural analysis of the modified Nafion membrane was conducted using Scanning Electron Microscopy (SEM). The SEM images provided critical insights into the surface morphology and the distribution of the silica nanolayer on the membrane surface.

As shown in Fig. 2a, the surface of the modified membrane is smooth and uniform, indicating a successful modification process. The presence of the silica nanolayer is visible, with no significant defects or discontinuities observed across the membrane surface. This uniformity ensures the membrane's consistent electrochemical performance and durability in practical applications.

The Energy-Dispersive X-ray Spectroscopy (EDX) mapping, presented in Fig. 2b, further confirmed the successful incorporation of the silica nanolayer. The EDX analysis revealed a homogeneous silicon (Si) distribution across the membrane surface, essential for enhancing the membrane's stability and electrochemical activity. The uniform distribution of Si suggests that the modification process was well-controlled, ensuring the desired properties of the membrane were achieved.

These microstructural findings provide a strong foundation for the subsequent electrochemical studies, indicating that the modified membrane possesses the necessary structural integrity and uniformity to perform effectively in the targeted applications.

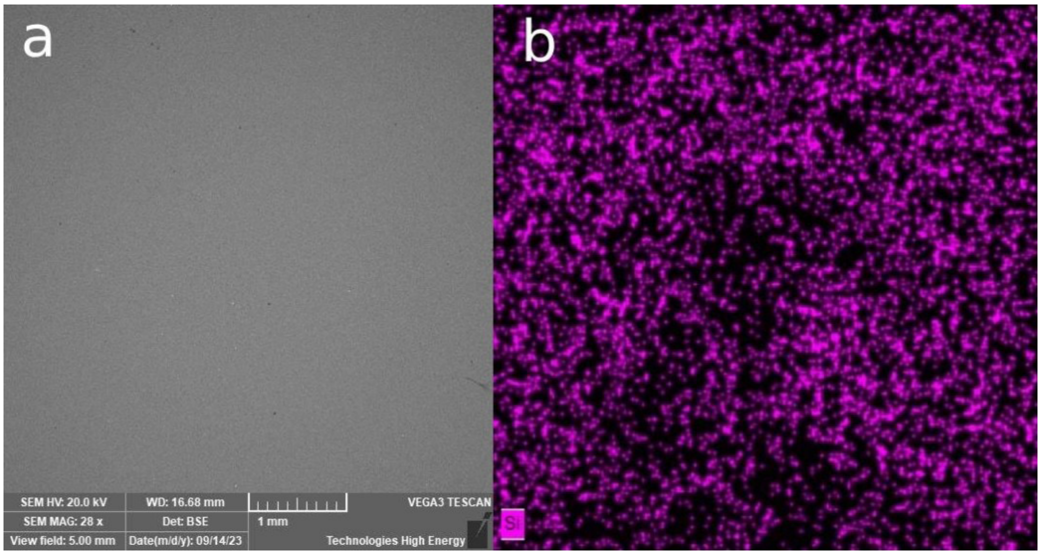

Fig. 2. (a) SEM image of the modified Nafion membrane surface. (b) EDX mapping illustrating the incorporation of Si (silicon) across the membrane surface.

Cyclic stability testing

The cyclic stability of the rebalancing cell is a critical parameter that determines the longevity and reliability of the energy storage system. This study analyzed the rebalancing cell's cyclic stability equipped with unmodified and modified Nafion membranes. The results are illustrated in Fig. 3, demonstrating the modified membranes' superior performance.

The cyclic stability tests involved subjecting the rebalancing cells to multiple discharge cycles, during which the cell voltage was continuously monitored. This approach allowed us to assess how well the membrane maintains its functionality over repeated cycles.

The rebalancing cell using the unmodified Nafion membrane showed stable performance for up to three consecutive cycles. However, after the third cycle, the cell's voltage declined sharply, indicating a loss of membrane integrity. This degradation suggests that the unmodified membrane is susceptible to chemical and mechanical stresses during cycling, leading to a breakdown in its ability to effectively balance the cell's operation.

In contrast, the rebalancing cell equipped with the modified Nafion membrane exhibited significantly enhanced cyclic stability. The cell could sustain stable operation for up to 10 consecutive cycles, representing a threefold improvement over the unmodified membrane. The consistent voltage profile across these cycles indicates that the membrane modification process, which involves the incorporation of a silica nanolayer via TEOS treatment, effectively reinforces the membrane structure and prevents degradation during repeated cycling.

Analysis of ECSA reduction

The impact of the TEOS-modified Nafion membrane on the platinum catalyst's electrochemically active surface area (ECSA) was assessed using cyclic voltammetry (CVA). The results of the CVA tests are presented in Fig. 4, comparing the platinum catalyst's initial and post-operation states with both the unmodified and modified membranes.

As seen in Fig. 4a, the CV curves for the cell using the unmodified Nafion membrane indicate a

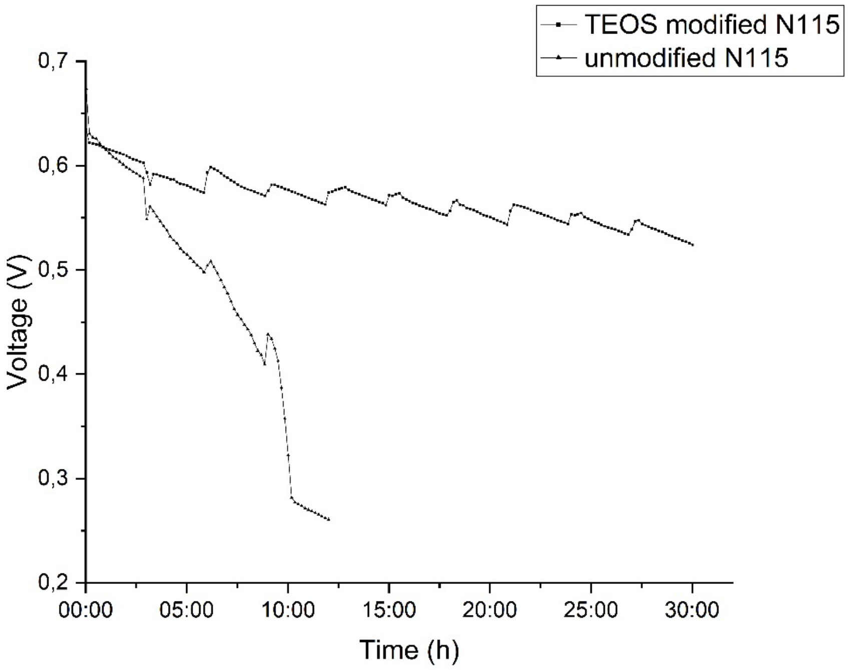

Fig. 3. Voltage stability of the rebalancing cell during cyclic stability testing for TEOS-modified Nafion N115 and unmodified Nafion N115 membranes.

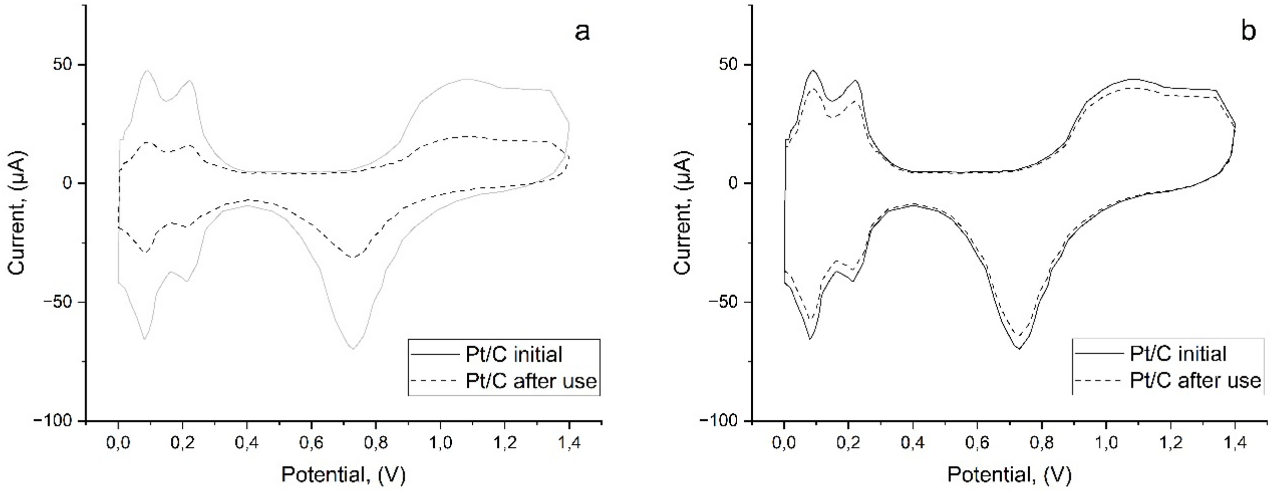

Fig. 4. Cyclic voltammograms comparing the electrochemically active surface area (ECSA) of Pt/C catalysts before and after use in rebalancing cells with (a) unmodified Nafion N115 membrane and (b) TEOS-modified Nafion N115 membrane.

significant reduction in the current response after cycling, particularly in the hydrogen adsorption/desorption regions (0 to 0.4 V). This reduction suggests a considerable loss of ECSA, which indicates catalyst degradation. The diminished current response is likely due to the crossover of electrolyte components, such as Fe^{2+}, Fe^{3+}, and Cl^- ions, through the unmodified membrane. These ions can interact with the platinum catalyst, leading to its poisoning and reducing the number of active sites available for electrochemical reactions.

In contrast, Fig. 4b shows the CV curves for the cell using the TEOS-modified Nafion membrane. Although there is still some reduction in the ECSA, as evidenced by the decrease in the current response, the loss is significantly less pronounced than with the unmodified membrane. The modified membrane's ability to limit the crossover of harmful ions results in better preservation of the catalyst's active surface area.

The observed differences in ECSA between the two membrane types highlight the effectiveness of the TEOS modification in protecting the platinum catalyst from degradation. The TEOS-modified membrane acts as a barrier, reducing the permeation of electrolyte components that can lead to catalyst poisoning. This protective effect is crucial for maintaining the catalyst's activity over prolonged operation, particularly in environments where the membrane is subjected to frequent cycling.

The reduction in ECSA for the unmodified membrane, as shown in Fig. 4a, clearly indicates the detrimental impact of ion crossover on catalyst performance. In comparison, the TEOS-modified membrane (Fig. 4b) demonstrates its ability to maintain a higher level of catalyst activity, which directly translates to improved cell performance and durability.

The enhanced cyclic stability observed with the modified Nafion membrane can be attributed to several critical factors introduced by the TEOS-based modification:

The TEOS modification forms a silica matrix within the Nafion membrane, which acts as a reinforcing agent. This matrix stabilizes the membrane's structure, reducing the extent of swelling and mechanical deformation that typically occurs during repeated cycling. The result is a membrane that can withstand the stresses associated with prolonged operation without significant degradation [11].

The silica matrix also decreases the membrane's permeability to multivalent ions, such as Fe^{2+} and Fe^{3+}, which are known to contribute to membrane and catalyst degradation. By limiting the diffusion of these ions, the modified membrane experiences less internal corrosion and chemical degradation, extending its operational lifespan [12].

Despite the reduced permeability to damaging ions, the TEOS modification does not hinder the transport of protons (H^+). Proton conductivity is crucial for maintaining the cell's electrochemical functionality, and the modified membrane's selective permeability ensures that proton transport remains efficient throughout the cycling process [13].

One of the most significant benefits of the modified membrane is its ability to reduce the crossover of electrolyte components, particularly ions such as Fe^{2+}, Fe^{3+}, and Cl^{-}, which can poison the catalyst in the membrane-electrode assembly [14 - 16]. By preventing these ions from migrating through the membrane, the modified Nafion membrane helps to preserve the electrochemically active surface area (ECSA) of the catalyst, reducing the rate of catalyst degradation.

The cyclic stability tests demonstrate that modifying Nafion membranes with TEOS significantly enhances their durability and performance in rebalancing cells. The modified membranes sustained 10 consecutive cycles without significant degradation, a substantial improvement over the unmodified membranes, which only sustained 3 cycles. This enhanced stability is primarily due to the structural reinforcement provided by the silica matrix and the reduced permeability to damaging ions, which collectively contribute to a more robust and long-lasting membrane.

Long-term durability testing

A long-term durability test was conducted to assess further the TEOS-modified Nafion N115 membrane's durability and reliability. This test involved 36 consecutive cycles, with each cycle lasting 4 h, over a total duration of 144 h. The results of this extended testing are shown in Fig. 5.

The voltage profile of the rebalancing cell equipped with the TEOS-modified Nafion membrane remained remarkably stable throughout the 144 h testing period. As illustrated in Fig. 5, the cell maintained a consistent voltage, with only minor fluctuations observed during the transition between cycles. This stability indicates that the modified membrane can sustain prolonged operation without significant degradation in performance.

Throughout the test, the membrane demonstrated high resilience to the operational stresses associated with repeated cycling. The absence of a significant decline in voltage over the 36 cycles suggests that the structural reinforcement provided by the TEOS modification effectively mitigates the common issues of membrane swelling, mechanical deformation, and ion crossover, which often lead to performance deterioration

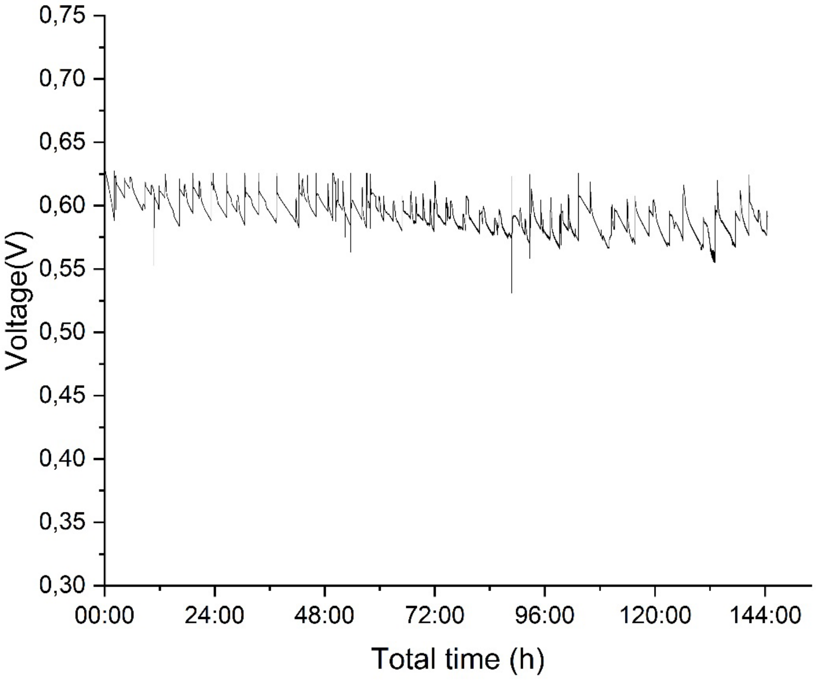

Fig. 5. Voltage stability during long-term durability testing of the rebalancing cell equipped with a TEOS-modified Nafion N115 membrane.

in unmodified membranes.The results of the long-term durability test highlight several critical aspects of the TEOS-modified membrane's performance:

The membrane's ability to maintain a stable voltage profile over 140 h of continuous cycling underscores its suitability for applications that demand long-term reliability and consistent performance. This is particularly important in energy storage systems, where membrane failure can lead to significant operational inefficiencies.

The minimal fluctuations in voltage throughout the test period indicate that the membrane experiences little to no significant degradation, even under extended operational conditions. This is a crucial advantage over unmodified membranes, which typically exhibit a gradual decline in performance over time.

The results reaffirm the earlier findings from the cyclic stability tests, further demonstrating the effectiveness of the TEOS modification in enhancing the membrane's durability. Reduced permeability to damaging ions improved structural integrity, and preserved proton conductivity contributes to the membrane's ability to withstand the rigors of long-term operation.

CONCLUSIONS

This study comprehensively evaluated the impact of TEOS modification on Nafion N115 membranes, focusing on their microstructural properties, cyclic stability, electrochemical activity, and long-term durability in rebalancing cells. The following conclusions can be drawn from the findings:

The TEOS modification process successfully incorporated a uniform silica nanolayer into the Nafion membrane, as confirmed by SEM and EDX analysis. This modification provided significant structural reinforcement, resulting in a smooth, uniform, and free of substantial defects membrane surface. This enhanced microstructural integrity is crucial for ensuring consistent performance in electrochemical applications.

The cyclic stability tests demonstrated that the TEOS-modified Nafion membrane significantly outperforms the unmodified Nafion membrane in rebalancing cells. The modified membrane sustained stable operation for up to 36 consecutive cycles, compared to only 3 cycles for the unmodified membrane. This improvement is primarily attributed to the structural reinforcement provided by the silica matrix, which reduces mechanical deformation and limits the crossover of damaging ions.

Cyclic voltammetry analysis revealed that the TEOS-modified membrane effectively preserves the platinum catalyst's ECSA, mitigating the loss of catalytic activity commonly observed with unmodified membranes. The modification limits the permeation of harmful ions such as Fe^{2+}, Fe^{3+}, and Cl^{-}, which can poison the catalyst and degrade its performance. As a result, the modified membrane helps maintain high catalytic activity over extended operation.

The long-term durability testing over 144 h (36 cycles of 4 h each) showed that the TEOS-modified Nafion membrane maintains a consistent voltage profile, with minimal degradation observed throughout the testing period. This indicates that the modified membrane can withstand prolonged operational stresses, making it a reliable choice for applications that require long-term stability and performance.

Despite incorporating the silica nanolayer, the TEOS-modified membrane maintains high proton conductivity, which is essential for efficient electrochemical performance. The membrane's selective permeability ensures that protons are effectively transported while harmful multivalent ions are restricted, further enhancing its operational lifespan.

The findings of this study highlight the potential of TEOS-modified Nafion membranes to significantly enhance the durability and performance of electrochemical systems, particularly in energy storage and conversion applications. The modifications not only improve the structural and electrochemical properties of the membranes but also offer a practical solution to the challenges of membrane degradation over time.

Future work could explore applying this modification technique in other membranes and electrochemical systems and investigate the long-term effects of TEOS modification under varying environmental and operational conditions. Additionally, further studies could optimize the modification process to maximize the benefits while minimizing any potential drawbacks, such as increased manufacturing complexity or cost.

Authors' contributions: *Y.K.: Conceptualization, Methodology, Investigation, Writing - original draft; O.K.: Supervision, Formal analysis, Validation; O.L.: Visualization, Writing - review and editing.*

REFERENCES

1. Y. Qi, S. Ma, F. Jin, D. Zhou, R. Li, Optimal dispatch of concentrating solar thermal power (CSP)-wind combined power generation system, J. Phys. Conf. Ser., 2636, 1, 2023, 012045.
2. C. Doetsch, J. Burfeind, Vanadium redox flow batteries, Storing Energy, 2016, 227-246.
3. A.K. Manohar, S. Malkhandi, B. Yang, C. Yang, G.K.S. Prakash, S.R. Narayanan, A high-performance rechargeable iron electrode for large-scale battery-based energy storage, J. Electrochem. Soc., 159, 8, 2012, A1209-A1214.
4. S. Wang, L. Ma, S. Niu, S. Sun, Y. Liu, Y. Cheng, A double-ligand chelating strategy to iron complex anolytes with ultrahigh cyclability for aqueous iron flow batteries, Angew. Chem. Int. Ed., 63, 9, 2024.
5. V. Watson, E.E. Effiong, E.E. Kalu, Influence of mixed electrolyte on the performance of iron-ion/hydrogen redox flow battery, ECS Electrochem. Lett., 4, 7, 2015, A72-A75.
6. S. Selverston, R.F. Savinell, J.S. Wainright, In-tank hydrogen-ferric ion recombination, J. Power Sources, 324, 2016, 674-678.
7. B.S. Jayathilake, E.J. Plichta, M. Hendrickson, S.R. Narayanan, Improvements to the coulombic efficiency of the iron electrode for an all-iron redox-flow battery, J. Electrochem. Soc., 165, 9, 2018, A1630-A1638.
8. K.L. Hawthorne, T.J. Petek, M.A. Miller, J.S. Wainright, R.F. Savinell, An investigation into factors affecting the iron plating reaction for an all-iron flow battery, J. Electrochem. Soc., 162, 1, 2014, A108-A113.
9. K.A. Mauritz, R.M. Warren, Microstructural evolution of a silicon oxide phase in a perfluorosulfonic acid ionomer by an in-situ sol-gel reaction. 1. Infrared spectroscopic studies, Macromolecules, 22, 4, 1989, 1730-1734.
10. R. Sharma, S. Gyergyek, S.M. Andersen, Critical thinking on baseline corrections for electrochemical surface area (ECSA) determination of Pt/C through H-adsorption/H-desorption regions of a cyclic voltammogram, Appl. Catal. B-Environ., 311, 2022, 121351.
11. J. Drillkens, D. Schulte, D.U. Sauer, Long-term stability of Nafion hybrid membranes for use in vanadium redox flow batteries, ECS Trans., 28, 30, 2010, 167-177.
12. G. Ye, C.A. Hayden, G.R. Goward, Proton dynamics of Nafion and Nafion/SiO_2 composites by solid-state NMR and pulse field gradient NMR, Macromolecules, 40, 5, 2007, 1529-1537.
13. M.A. Ashraf, A. Islam, M.A. Butt, H.A. Mannan, R.U. Khan, K. Kamran, S. Bashir, J. Iqbal, A.A. Al-Ghamdi, A.G. Al-Sehemi, Quaternized diaminobutane/poly(vinyl alcohol) cross-linked membranes for acid recovery via diffusion dialysis, Membranes, 11, 10, 2021, 786.
14. T.M. Arruda, B. Shyam, J.M. Ziegelbauer, S. Mukerjee, D.E. Ramaker, Investigation into the competitive and site-specific nature of anion adsorption on Pt using in situ X-ray absorption spectroscopy, J. Phys. Chem. C, 112, 46, 2008, 18087-18097.
15. M. Goor-Dar, N. Travitsky, E. Peled, Study of hydrogen redox reactions on platinum nanoparticles in concentrated HBr solutions, J. Power Sources, 197, 2012, 111-115.
16. R. Devivaraprasad, T. Kar, P. Leuaa, M. Neergat, Recovery of active surface sites of shape-controlled platinum nanoparticles contaminated with halide ions and its effect on surface structure, J. Electrochem. Soc., 164, 9, 2017, H551-H560.