

Interfacial stabilization of Nafion membrane with graphene and PTFE: A path to more durable polymer electrolyte membrane water electrolyzers

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ABSTRACT Stability and durability of electrochemical energy conversion systems are significant issues. In this study, two stabilization strategies were investigated: 1) the application of few-layer graphene as a barrier layer on both sides of the Nafion membrane, and 2) the incorporation of polytetrafluoroethylene directly into the catalyst layers. Electrochemical performance was assessed in a two-electrode configuration: potentiostatic aging at 2.5 V and hydrogen crossover measurements. The characterization of materials functioning as barrier layers was conducted using scanning and transmission electron microscopy, laser correlation spectroscopy, and differential thermal analysis. It is shown that both components stabilize Nafion through interfacial interactions, resulting in a longer service life and reduced hydrogen crossover. While the reference sample showed increased crossover, the modified samples exhibited reductions of 50% and 33%. These findings underscore the potential of the studied materials in enhancing the stability of polymer electrolyte membrane water electrolyzers, contributing to the advancement of more durable and efficient systems for hydrogen energy applications.

KEYWORDS graphene; PTFE; stabilized Nafion; membrane-electrode assemblies; water electrolyzer.

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1. Introduction

The development and industrial implementation of electrochemical energy conversion devices with a proton exchange membrane is currently an intensively developing field [1]. Among these devices are water electrolyzers [2–5]. One of the important aspects that determines the competitiveness of a device in the economy is the reliability (stability and long-term operation). Problems related to the durability, stability, and safety of such systems are currently being addressed in many research facilities around the world. These issues have not yet been fully resolved. Norazahar et al. [6] noted that the reliability aspect is critical to ensure safe production of hydrogen as a fuel. Efficient hydrogen production depends on the reliability of electrolyzers. Polymer electrolyte membrane water electrolyzer (PEMWE) is one of the most promising technologies for hydrogen production. However, properties such as hydrogen solubility, diffusion coefficient, and the partial pressure differential between flow channels may influence the reliability and safety of the system. Operating conditions may also lead to safety issues within the PEMWE due to membrane degradation or thinning. The damaged membrane initiates the migration of hydrogen into the anode space and may lead to an explosion. Hydrogen crossover through even an undamaged membrane also plays a significant role in the performance of the electrolyzer, as it reduces its efficiency. Shirvanian et al. [7] highlighted that degradation is a significant issue in the use of PEMWEs. Research and development of new components are likely to result in outcomes in the long-term perspective. In the short term, it is crucial to be able to produce high-performance, cost-effective PEMWE systems with a long service life based on existing technologies. In the referenced article, the authors investigate the impact of operating conditions on the longevity of the electrolyzer. They conclude that one of the most effective approaches for ensuring extended and safe operation is to maintain “soft” operating conditions, including low temperatures and pressures, low overpotentials, and current densities. Moreover, it is noted that dispersing the Ir catalyst on stable support materials (such as carbides or nitrides of transition metals) may enhance the catalyst’s durability.

One of the key factors affecting the long-term performance of a PEMWE is the degradation of the proton exchange material (membrane and ionomer in the electrode layer) [7–9]. Papakonstantinou et al. [10] pointed out the excellent stability of the anodes in modern electrolyzers, as well as the instability of the proton exchange membrane, which constrains the device's service life. For proton exchange membrane fuel cells (PEMFCs) extensive research has been conducted, resulting in various types of hybrid composite membranes based on Nafion®, such as Nafion®/inorganic fillers, Nafion®/ionic liquid, and other modified Nafion® membranes [11]. Despite some achievements, the search for new compositions to increase the longevity and performance of membranes continues, as evidenced by the emergence of new publications on this topic.

To address ionomer degradation, the most commonly used stabilization approaches are reinforcement and filling of the membranes:

1. reinforcement refers to the creation of a coating or matrix that enhances mechanical stability [12–14];
2. filling refers to the introduction of inorganic additives that improve chemical stability [15–17].

Jaio et al. [14] used polytetrafluoroethylene (PTFE) as a reinforcing material. The PTFE-Nafion membrane features low cost, high mechanical strength, and minimal swelling.

The use of fillers to create composite (filled) membranes has proven to be an effective way to enhance water loss resistance and thermal stability [16]. Ibrahim et al. [16] presented the key approaches to modifying ion-exchange materials, primarily focusing on the creation of hybrid membranes containing nanoparticles of inorganic materials. They highlighted that the main factor contributing to the enhanced conductivity and selectivity of hybrid membranes is the change in pore and channel structures and the distribution of carrier concentrations.

When creating stabilized composites based on perfluorinated polymers with sulfonic groups (Nafion – an ionomer with long side chains in the molecule, Aquivion – an ionomer with short side chains, and related ionomers), materials containing few-layer graphene (G) as a stabilizer have proven to be effective [18–20]. As shown in these works, stabilization of the ionomer occurs due to the formation of surface compounds of the polymer on G.

Graphene and graphene-based materials are of significant interest due to their unique structure and properties. These materials possess a two-dimensional structure and can exist in various forms, differing in both the number of layers and the presence of surface functional groups, which can be precisely controlled, for instance, during electrochemical synthesis [21,22]. For example, reference [22] presents comparative results for producing graphene with tailored characteristics using various methods, including ultrasonic dispersion at different power levels and electrochemical exfoliation under various conditions. The study reports the feasibility of synthesizing few-layer (1-3 layers) graphene with a tunable oxygen content, dependent on the processing parameters. Graphene materials are unique substances with an easily tunable pseudo-2D structure and modifiable surface functional group composition. This tunability offers significant flexibility for designing composite membranes. Furthermore, graphene exhibits selective permeability: it is permeable to protons while being impermeable to most other substances, including gases, fuels, and oxidizers. Its incorporation into membranes significantly reduces reactant crossover. In [23], the effect of incorporating various forms of carbon nanomaterials as additives into Nafion membranes on the performance of direct methanol fuel cells (DMFCs) was investigated. The study demonstrated that carbon nanomaterials substantially influence the development of polymer electrolytes for DMFCs. The performance of the composite membrane electrolyte depends on the choice of carbon nanomaterial, such as two-dimensional graphene oxide (GO), one-dimensional carbon nanotubes (CNTs) or carbon nanofibers (CNFs/GNFs), and fullerenes. The structural orientation and composition of these carbon materials within the polymer matrix significantly affect the membrane's properties. Surface functionalization of these nanomaterials imparts hydrophilicity, fine-tunes the composite's conductivity, and enhances interfacial adhesion with the polymer matrices. For Nafion® membranes, GO has been identified as a particularly suitable nanofiller, especially where reducing methanol permeability is critical; the planar sheet structure of graphene-based materials is more effective than the tubular structure of CNTs in mitigating fuel crossover.

It is important to note that most published studies focus on the stability of the membranes, while little attention has been paid to the stability of the ionomer distributed in the electrode layer. To a certain extent, this can be viewed as a serious gap in addressing the issue of electrochemical system stability, since even with a stable membrane, the electrodes must also be functional.

The aim of this work was to investigate and compare the efficiency of two distinct approaches to stabilize the MEA: i) applying a barrier layer of few-layer graphene directly onto the Nafion membrane, and ii) incorporating PTFE as a stabilizer within the catalyst layers to reinforce the Nafion ionomer. The primary object of the study is the membrane-electrode assembly (MEA) as a whole, with a focus on mitigating hydrogen crossover and improving durability. A key outcome of this study is the demonstration that the graphene barrier layer provides superior mitigation of hydrogen crossover, halving it after aging, thereby offering a more promising path to durable PEM electrolyzers.

2. Experimental Section

2.1. MEA Fabrication

Platinized carbon black (Pt/C) was used as both a cathode and an anode catalyst. The selection of platinum over iridium for the anode was made to speed up the degradation process of the electrolyzer and to carry out real-time operation tests, as opposed to using accelerated stress tests (AST).

A 2% aqueous solution of Nafion, prepared by diluting a 10% stock solution of Nafion DE1021 (DuPontTM, Wilmington, DE, USA), was used. An aqueous dispersion of PTFE (OJSC “Plastpolymer”, St. Petersburg, Russia) with a spherical particle size of 250–400 nm was used. Thermally expanded graphite (TEG) was used as a precursor for G fabrication. TEG was obtained from NPO “Graphene Materials” LLC, St. Petersburg, Russia. The technology of synthesis is described in [24]. Commercial platinized carbon black (40% Pt) from E-TEK was used as the electrocatalyst. Isopropanol (99.80%, ECOS-1 JSC), and deionized water with resistivity at room temperature $\rho \geq 18 \text{ MOhm} \times \text{cm}$ were used. A solution of H₂O₂, grade 8–4 (Lega LLC, Dzerzhinsk, Russia) was used.

To study the physicochemical properties and fabricate membrane-electrode assemblies (MEAs), component dispersions were initially prepared in an isopropanol-water medium with a 1:1 volume ratio. The samples were prepared by mixing accurately weighed components and then subjected to ultrasonic treatment for 40 hours in a Branson 3510 ultrasonic bath (Branson Ultrasonics Corporation, Danbury, CT, USA).

MEAs were prepared by depositing a homogeneous dispersion of components directly on a PEM through a stainless-steel mask. The catalyst inks for the electrodes were applied by hand brushing directly onto the membrane (or onto the graphene barrier layer for the MEA G-layer). Prior to the deposition of the electrode material, the membrane was treated in 3% H₂O₂ solution for 10 min at a temperature of 70–80°C, followed by immersion in 0.5 M sulfuric acid for 15 min at a temperature of 70–80°C, and then was washed five times with deionized water. The electrodes were prepared by depositing of prepared composite dispersions containing Pt on a PEM of Nafion 212 type, MF-4SK (OJSC “Plastpolymer”, St. Petersburg, Russia), of thickness 50 μm . The membrane was thermostated at 85°C on an Ika C-MAGPH 7 wafer (IKA-Werke GmbH & Co. KG, Staufen, Germany) with a heat controller. The amount of the deposited material was monitored gravimetrically.

Three types of MEAs were fabricated: a standard MEA (reference), a MEA with a G barrier layer, and a MEA with a PTFE barrier layer (Table 1).

TABLE 1. Composition of samples used for the study

Type of sample	Composition, wt%			MEA Cathode/Anode Pt loading, mg/cm ²	Barrier layer
	Nafion	Pt/C (40% Pt)	PTFE		
Reference MEA	20	80	–	0.23/ 0.20	–
MEA PTFE-layer	20	60	20	0.29/ 0.31	+
MEA G-layer	20	80	–	0.23/ 0.27	+

G barrier layers were first deposited on both sides of the membrane via airbrushing, with a layer thickness of ~ 0.5 – $1 \mu\text{m}$. Subsequently, the catalyst layers were applied. The barrier ink was formulated by dispersing thermally expanded graphite (TEG) in a 2% Nafion solution using an isopropanol/water (1:1 vol) medium. The total loading of the dry barrier layer was 0.01 mg/cm², corresponding to a graphene (TEG) loading of 0.008 mg/cm² and a Nafion loading of 0.002 mg/cm². The PTFE barrier layers were applied to both sides of the membrane by spreading a dispersion (Pt/C-Nafion-PTFE). Following the assembly, all MEAs underwent a final conditioning step to activate proton conductivity by boiling in 0.5 M H₂SO₄ for 1 hour, followed by thorough rinsing with deionized water.

2.2. Microscopic Studies

Target-oriented approach was utilized for the optimization of the analytic measurements [25]. Before measurements the samples were mounted on a 3 mm copper grid and fixed in a grid holder. Samples morphology was studied using Hitachi SU8000 (Hitachi High-Tech Corp., Tokyo, Japan) field-emission scanning electron microscope (SEM). Images were acquired in bright-field STEM mode at 30 kV accelerating voltage.

2.3. Energy-Dispersive X-ray Spectroscopy

EDX measurements were carried out using the FEI Quanta 200 scanning electron microscope (FEI Company, Hillsboro, OR, USA).

2.4. Study of particle size using laser correlation spectroscopy

The particle study was conducted using a Zetasizer Nano ZS analyzer (Malvern Panalytical, Malvern, United Kingdom) at a temperature of 25°C. The dispersion medium was a mixture of isopropanol and water in a 1:1 volume ratio. The following parameters of the dispersion medium and material were used:

- Refractive index of the dispersion medium: 1.359;
- Refractive index of the material (Nafion): 1.35;
- Viscosity of the dispersion medium: 2.5966 mPa·s;
- Absorption coefficient of the material (Nafion): 0.

A He–Ne laser with a wavelength of 632.8 nm was used as the light source. The Smoluchowski equation was applied to calculate the zeta potential.

2.5. Differential thermal studies

The study of thermal degradation was carried out on a derivatograph of Mettler Toledo TGA/DSC 1 type with the software STARe System (Mettler-Toledo LLC, Columbus, OH, USA) with blowing air through the derivatograph chamber at a rate of 30 cm³/min in the mode of uniform temperature rise at a rate of 10 K/min in the temperature range $T = 35\text{--}1000^\circ\text{C}$. A sample of material weighing a few mg was placed in an alund crucible, and mass and thermal curves were recorded during heating. Dispersions for the study were evaporated, poured onto a glass substrate and dried at a.c. to air-dry (~40–50% relative humidity), and then the dry residue was removed with a metal (stainless steel) spatula.

2.6. Electrochemical study

The electrochemical characteristics of the MEAs were studied in two modes: fuel cell mode and electrolyzer mode, implemented in a two-electrode configuration. The MEAs were placed in Heliocentris cells (Heliocentris Academia International GmbH, Berlin, Germany). Measurements were performed using an Elins P-40X potentiostat (Elins LLC, Chernogolovka, Russia).

Hydrogen crossover was measured by linear sweep voltammetry following a previously described method [26]. N₂/H₂ were passed through the electrodes. The working electrode was scanned at a rate of 4 mV/s from 0 V to 0.8 V. Experiments were conducted at room temperature and atmospheric pressure. Measurements were taken before and after aging.

MEA aging was carried out in electrolyzer mode applying a constant voltage of 2.5 V for 145 h. The MEA was placed in an electrolyzer cell, filled with water, and the required voltage was applied via the potentiostat. The experiments were performed at room temperature and atmospheric pressure.

3. Results and Discussion

Fig. 1 shows micrographs of the composite system: G-Nafion-Pt/C. The figure demonstrates that platinized carbon black is positioned on the surface of G sheets. The TEM image shows black dots corresponding to platinum nanoparticles distributed on the surface of carbon black (lighter spherical particles). In the TEM image, the G sheet exhibits increased transparency, which corresponds to its thin structure. The G edges are distinguishable in the images, appearing as bright stripes in the SEM image and darker stripes in the TEM image. An approximate evaluation of the thickness of the bright edges marked by yellow arrows, corresponding to the edges of graphene sheets, indicates a size of less than 10 nm. Fig. 1(d) shows a homogeneous structure, uniform over hundreds of nanometers, composed of evenly distributed spherical and semi-spherical features. No graphene sheets are present. The feature size is primarily in the ~100–300 nm range, characteristic of PTFE. Smaller features (<100 nm) are attributed to spherical platinum/carbon black particles.

3.1. Particle size analysis

Fig. 2 illustrates the particle size distributions for dispersions of different systems containing the Nafion ionomer, PTFE, and few-layer G as the dispersed phase. The PTFE-Nafion system demonstrates relatively narrow distributions with a single peak, whereas the G-Nafion sample exhibits a polydisperse nature with multiple peaks over a broad size range, which may be associated with the polydispersity of few-layer G.

In the case of pristine Nafion sample (6.7 g/L), the particle size distribution spans approximately 0.4–1.8 nm for both volume and number distributions, with maxima at 0.8 nm (v) and 0.7 nm (n). A zeta potential of -39 ± 3 mV was recorded, reflecting the good stability of the dispersion. For pristine PTFE (6.7 g/L), the particle size distribution is broader, ranging from approximately 100 to 1000 nm in both volume-based and number-based measurements, with peaks at 342 nm (v) and 106 nm (n). The zeta potential of -6.4 ± 0.5 mV was measured, which is significantly lower than 30 mV in absolute value, indicating low dispersion stability. In the case of the PTFE-Nafion sample, with a concentration of 6.7 g/L for each component, the particle size range was found to be similar to that of pristine PTFE (~100–1000 nm). The maximum for the volume distribution of the PTFE-Nafion sample coincides with the maximum for pure PTFE (342 nm). The peak of the number-based distribution is displaced towards larger sizes, with a value of 142 nm. It should be noted that particles around 1 nm, typical for pristine Nafion in the ~0.4–1.8 nm range, are not present in the PTFE-Nafion

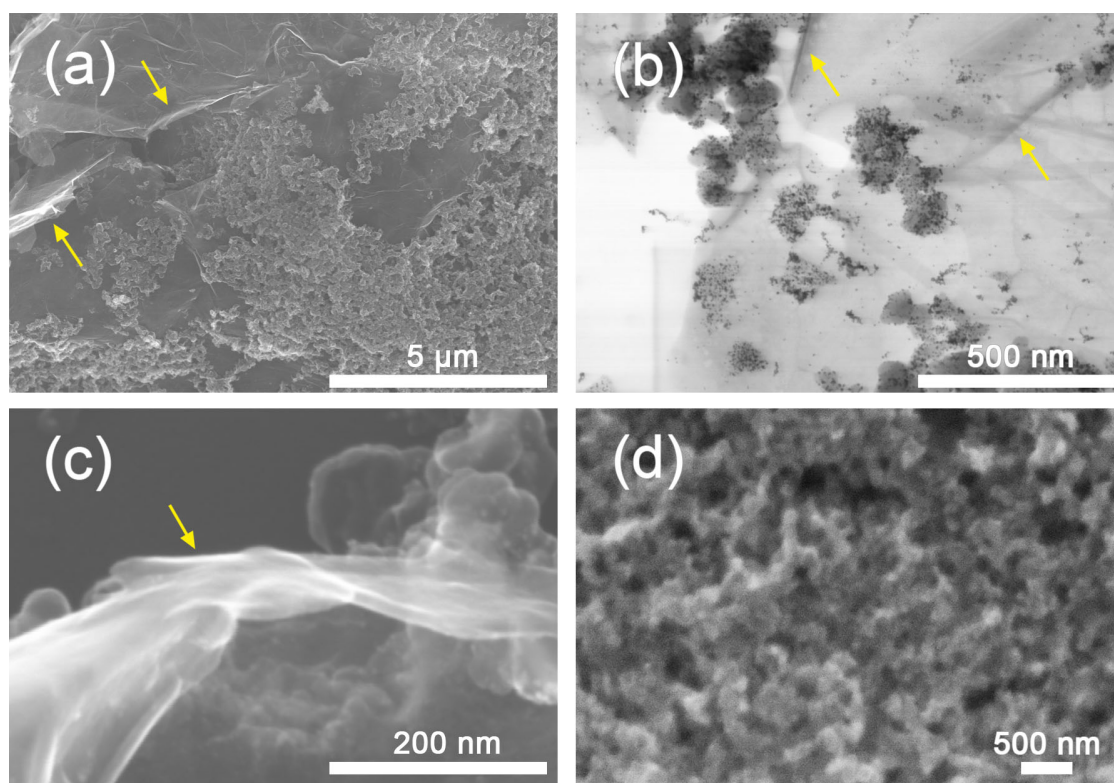


FIG. 1. Microstructure of the composite electrode materials: (a [18], c) SEM and (b) STEM images of the G-Nafion-Pt/C; (d) SEM image of the PTFE-Nafion-Pt/C

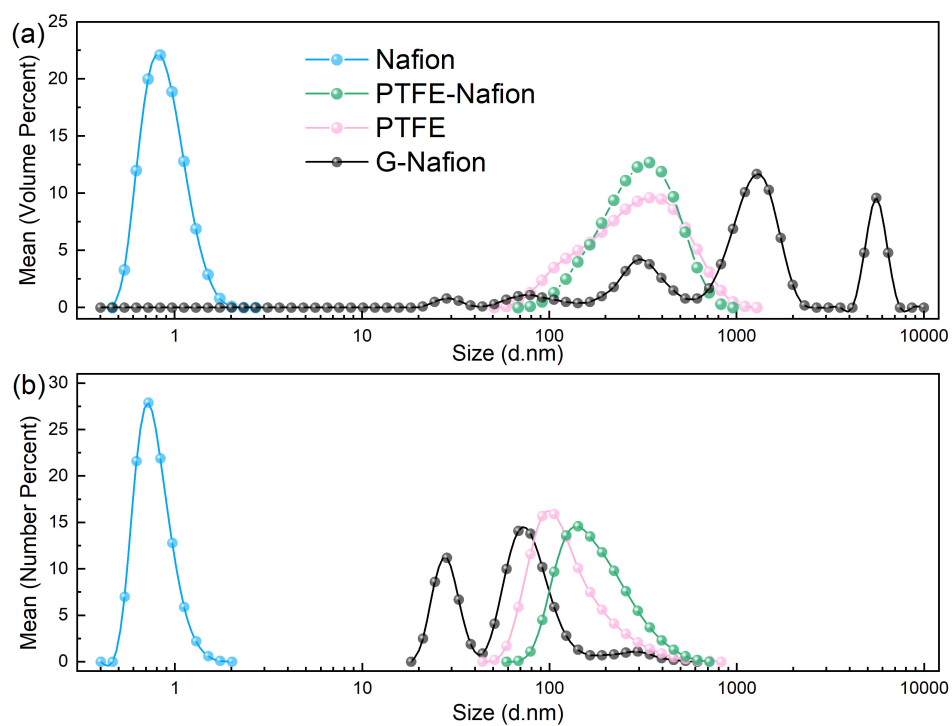


FIG. 2. Volume (a) and number (b) particle size distributions in an isopropanol-water medium with a 1:1 volume ratio for different dispersions: Nafion, PTFE, PTFE-Nafion, G-Nafion

sample. Additionally, the peak of the number-based particle size distribution shifts toward larger sizes compared to pristine PTFE. The shift in the peak of the number-based particle size distribution toward larger sizes compared to pristine PTFE, combined with the absence of ~ 1 nm Nafion particles, indicates the formation of a Nafion polymer coating on PTFE particles. For the G-Nafion dispersion with concentrations of 0.33 g/L (G) and 0.083 g/L (Nafion), multiple peaks are observed in the size ranges of approximately ~ 20 to ~ 7500 nm for the volume-based distribution and ~ 20 to ~ 600 nm for the number-based distribution. Particles in the ~ 1 nm range, which are characteristic of Nafion, are not present. It indicates that Nafion polymer adsorbs onto the G surface. The dispersion includes few-layer G particles with submicron sizes: 28, 68, and 295 nm. The volume-based distribution shows two maxima at approximately ~ 1300 and ~ 5600 nm. These larger particles are likely associated with the undispersed fraction of TEG. Nafion is located on the surface of G. The zeta potential of the particles is -76 ± 14 mV, which indicates excellent stability of the dispersion.

Thus, the particle size analysis of the binary dispersion systems revealed that Nafion is structurally associated with the second component and is located on the surface of its larger particles. The resulting dispersions exhibit a high zeta potential, greater than 30 mV, indicating their high stability.

3.2. Differential thermal studies

Fig. 3 shows a comparison of the derivatograms of the studied materials for the water electrolyzer: pristine Nafion, PTFE, and their composites. The thermal oxidative decomposition of pristine Nafion occurs in the temperature range of 260 – 504°C with several rate maxima. The lowest temperature maximum of the destruction rate associated with desulfurization of the molecule [27], is observed at 344°C . In the case of the G-Nafion composite, thermal decomposition initiates at higher temperatures, specifically within the 360 – 470°C range, with a single rate maximum occurring at 422°C . These results indicate the stabilization of the Nafion polymer and a change in its decomposition mechanism, aligning with previously reported data [18]. Higher temperature peaks in the mass loss rate are associated with G oxidation [18].

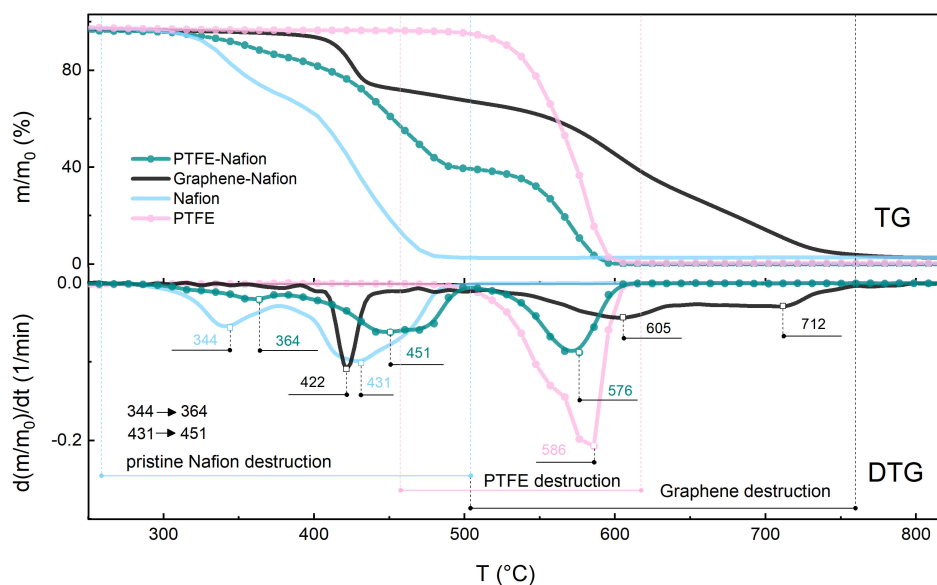


FIG. 3. Derivatograms of the electrode materials used in the electrolyzer. The heating rate is 10 K/min. TG – thermogravimetric curve, DTG – differential thermogravimetric curve

The thermal oxidative destruction of pristine PTFE occurs in a single stage within the temperature range of 457 – 617°C , with a maximum rate observed at 586°C . In the PTFE-Nafion composite, similar patterns are observed. However, Nafion in the composite undergoes decomposition differently than the pristine polymer: the onset of decomposition is shifted by 20°C toward a higher temperature region compared to pristine Nafion. The completion of Nafion decomposition coincides with the initiation of PTFE decomposition ($\sim 504^\circ\text{C}$). The maintained peak structure on the DTG curve for the PTFE-Nafion system suggests that the thermal decomposition mechanism of Nafion remains unchanged in the composite. The temperature shift toward higher values confirms the stabilization of Nafion through weak (adsorptive) interactions with the PTFE surface. These findings align with the particle size measurements.

Thus, the analysis of the derivatograms indicates that there is a strong interfacial interaction between the Nafion ionomer and G, with a weaker interaction observed between Nafion and PTFE. Nafion stabilizes on the surfaces of the materials, G and PTFE, which is consistent with the particle size analysis for these systems.

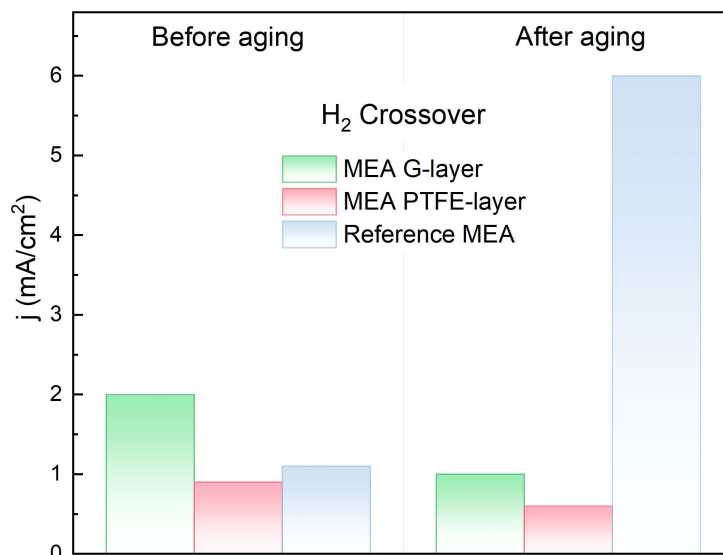


FIG. 4. H_2 crossover current density before and after aging of different samples

3.3. Investigation of Hydrogen Crossover Through the Membrane

Fig. 4 illustrates the hydrogen crossover current density before and after aging for three MEAs with varying electrode compositions: reference (Nafion-Pt/C), with PTFE as a stabilizer, and with a G barrier layer.

As shown in Fig. 4, the hydrogen crossover current density after aging was reduced by 50% (MEA G-layer) and 33% (MEA PTFE-layer) in the modified samples, indicating a substantial improvement in membrane performance. In contrast, the hydrogen crossover of the reference sample increased by approximately 5.5 times after aging.

It can be assumed that the mechanism for the reduction in hydrogen crossover during aging is related to structural changes in the near-surface layer of the membrane, which occur as a result of the aging process. This applies to both the graphene- and PTFE-modified samples, since in both cases, there is a strong interfacial interaction between Nafion and the additive. A similar effect is described in the scientific literature.

As shown in [28], the incorporation of graphene oxide (GO) into a Nafion membrane reduces acetone and hydrogen crossover in an acetone electrochemical hydrogenation cell. Impedance analysis confirmed the rearrangement of GO flakes during cell operation, reflected by a decrease in high-frequency resistance (HFR) and the interfacial resistance of the blocking interlayer after a continuous 15-hour electrochemical testing protocol. This observation is supported by transmission electron microscopy, which reveals structural changes within the GO interlayer.

Furthermore, in reference [29], rheological analysis of sulfonated graphene oxide (SGO) dispersions in a Nafion solution demonstrated a sharp increase in viscosity, peaking at an SGO content of 0.5%. The authors note that this indicates a strong interaction between the components at this specific ratio. As the SGO content increases further, particle agglomeration occurs, and the viscosity drops. The authors explain SGO's effect on crossover by two mechanisms: the steric factor of graphene particles and the formation of denser (and less permeable) ionomer structures in the presence of graphene compared to pure Nafion (see rheology data).

In our case, the reduction in hydrogen crossover during aging for MEAs with barrier layers can be explained by a structural reorganization of the membrane's near-surface layer adjacent to the graphene or PTFE. This likely involves partial penetration of the modifiers into this layer due to migration in the electric field and a resulting densification of the structure.

Thus, G and PTFE layers on Nafion membranes exhibit a barrier effect against undesirable fuel crossover, which is attributed to the interfacial interactions between the Nafion ionomer and the stabilizing materials. In the case of G, the interaction is realized through strong surface adsorption of the polymer chains, likely involving π - π stacking and van der Waals forces, leading to denser chain packing and increased thermal stability. For PTFE, the interfacial interaction is of a weaker, adsorptive nature, which nonetheless results in the formation of a polymer shell around PTFE particles, thereby reducing ionomer mobility and swelling. These interactions suppress hydrogen crossover and contribute to improved mechanical and chemical stability of the membrane-electrode assembly.

3.4. Polarization curves

Fig. 5 demonstrates the dynamics of polarization curves during the aging process. The pattern of change in the dependencies during the aging process of the reference sample differs from that of the modified MEAs. For the PTFE- and G-modified MEAs, an improvement in performance is observed at the beginning of operation, with an increase in current density. The improvement is attributed to the activation processes of the MEA, which involve the desorption of

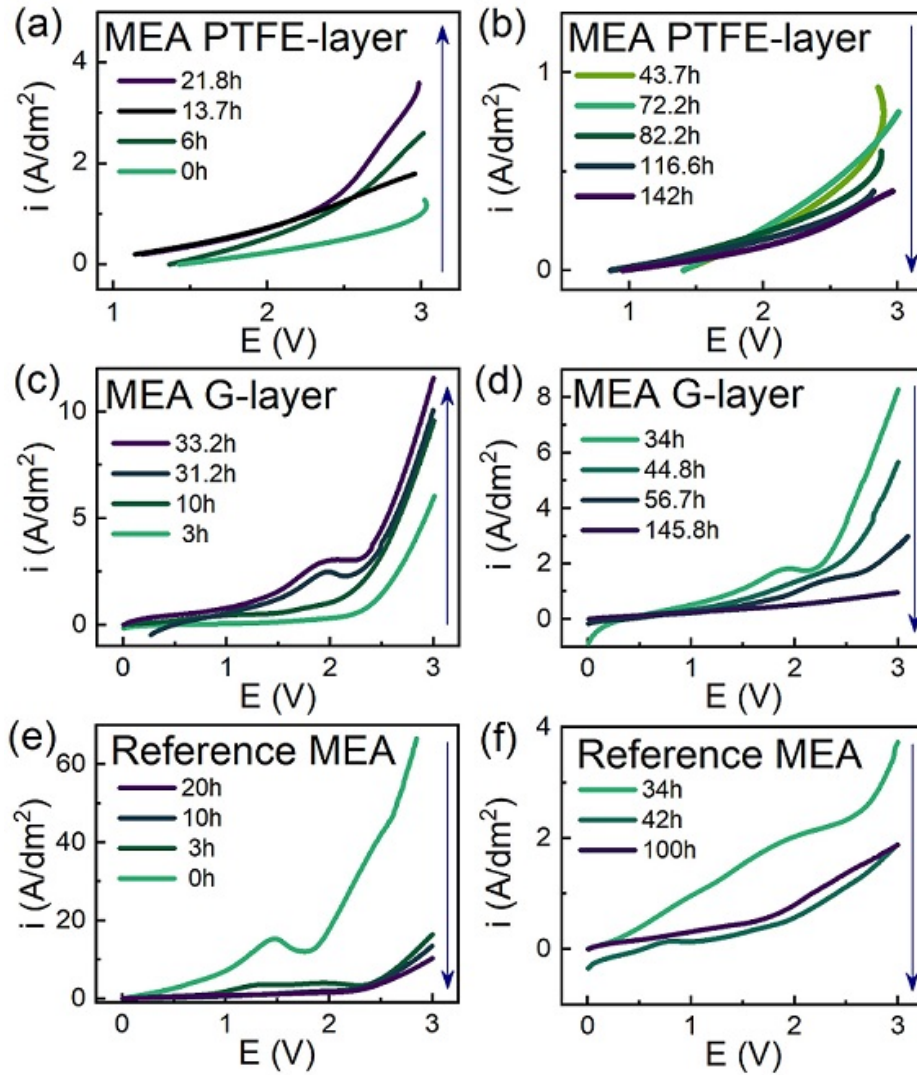


FIG. 5. Dynamics of polarization curves in electrolyzer mode during the aging of MEAs of various compositions under potentiostatic conditions at 2.5 V: PTFE-stabilized sample, performance improvement (a) and degradation (b) periods; G-stabilized sample, performance improvement (c) and degradation (d) periods; standard composition sample at the early stage of degradation (e) and at the end of operation (f); $t = 25^{\circ}\text{C}$, atmospheric pressure

impurities from the platinum surface, the hydration of the electrode layers and membrane, and the formation of charge and mass transfer channels [30] (Fig. 5a,c). Subsequently, deterioration of characteristics occurs (Fig. 5b,d), associated with degradation processes. In the case of the reference sample, high specific values are observed initially, followed by a sharp decline in performance (Fig. 5e), which then continues to decrease monotonically (Fig. 5f).

4. Conclusion

The stabilization of the proton-conducting polymer Nafion on the surfaces of nanostructured materials, such as few-layer G and PTFE, occurs through interfacial interactions between the G-Nafion and PTFE-Nafion components.

The G-Nafion system, achieved through ultrasonic dispersion of TEG, exhibits polydispersity, containing few-layer G particles with sizes in the submicron region (28, 68, 295 nm) and a small number of large TEG particles (around 1300 and 5600 nm) that remain undispersed. Nafion is positioned on the surface of G.

The PTFE-Nafion system is relatively monodisperse, and the Nafion polymer forms a coating on the surface of the PTFE particles.

The analysis of particle sizes in binary dispersions showed that Nafion is structurally integrated with the second component, positioning itself on the surface of the larger particles. The dispersions obtained exhibit a high zeta potential, greater than 30 mV, indicating their high stability.

Thermal analysis demonstrated the presence of interfacial interactions of different strengths between the components: a strong interaction between the Nafion ionomer and G, and a weaker one between Nafion and PTFE. Nafion stabilizes on the surfaces of these materials.

The modified MEAs show lower hydrogen crossover through the membrane in comparison with the standard sample after 145 h of aging at a constant voltage. The principal finding is that the application of a few-layer graphene barrier layer on the membrane surface is a more effective strategy than the incorporation of PTFE into the catalyst layers. This conclusion is quantitatively supported by the post-aging hydrogen crossover measurements, which showed a twofold reduction for the graphene-modified MEA compared to a 1.5-fold reduction for the PTFE-modified MEA.

References

- [1] de Sá M.H. Electrochemical Devices to Power a Sustainable Energy Transition—An Overview of Green Hydrogen Contribution. *Applied Sciences*, 2024, **14**(5), P. 2168.
- [2] Wang T., Cao X., Jiao L. PEM water electrolysis for hydrogen production: fundamentals, advances, and prospects. *Carbon Neutrality*, 2022, **1**(1), P. 21.
- [3] Shiva Kumar S., Himabindu V. Hydrogen production by PEM water electrolysis – A review. *Materials Science for Energy Technologies*, 2019, **2**(3), P. 442–454.
- [4] Thomassen M.S., Reksten A.H., Barnett A.O., Khoza T., Ayers K. PEM water electrolysis. In: *Electrochemical Power Sources: Fundamentals, Systems, and Applications*, Elsevier, 2022, P. 199–228.
- [5] Salehmin M.N.I., Husaini T., Goh J., Sulong A.B. High-pressure PEM water electrolyser: A review on challenges and mitigation strategies towards green and low-cost hydrogen production. *Energy Conversion and Management*, 2022, **268**, P. 115985.
- [6] Norazahar N., Khan F., Rahmani N., Ahmad A. Degradation modelling and reliability analysis of PEM electrolyzer. *International Journal of Hydrogen Energy*, 2024, **50**, P. 842–856.
- [7] Shirvanian P., van Berkel F. Novel components in Proton Exchange Membrane (PEM) Water Electrolyzers (PEMWE): Status, challenges and future needs. A mini review. *Electrochemistry Communications*, 2020, **114**, P. 106704.
- [8] Kuhnert E., Mayer K., Heidinger M., Rienessell C., Hacker V., Bodner M. Impact of intermittent operation on photovoltaic-PEM electrolyzer systems: A degradation study based on accelerated stress testing. *International Journal of Hydrogen Energy*, 2024, **55**, P. 683–695.
- [9] Phan T.T., Kim S.K., Islam J., Kim M.J., Lee J.H. Degradation analysis of polymer electrolyte membrane water electrolyzer with different membrane thicknesses. *International Journal of Hydrogen Energy*, 2024, **49**, P. 875–885.
- [10] Papakonstantinou G., Algara-Siller G., Teschner D., Vidaković-Koch T., Schlögl R., Sundmacher K. Degradation study of a proton exchange membrane water electrolyzer under dynamic operation conditions. *Applied Energy*, 2020, **280**, P. 115911.
- [11] Prykhodko Y., Fatyeyeva K., Hespel L., Marais S. Progress in hybrid composite Nafion®-based membranes for proton exchange fuel cell application. *Chemical Engineering Journal*, 2021, **409**, P. 127329.
- [12] Shi S., Weber A.Z., Kusoglu A. Structure/property relationship of Nafion XL composite membranes. *Journal of Membrane Science*, 2016, **516**, P. 123–134.
- [13] Shin S.H., Nur P.J., Kodir A., et al. Improving the Mechanical Durability of Short-Side-Chain Perfluorinated Polymer Electrolyte Membranes by Annealing and Physical Reinforcement. *ACS Omega*, 2019, **4**(21), P. 19153–19163.
- [14] Jao T.C., Jung G.B., Kuo S.C., Tzeng W.J., Su A. Degradation mechanism study of PTFE/Nafion membrane in MEA utilizing an accelerated degradation technique. *International Journal of Hydrogen Energy*, 2012, **37**(18), P. 13623–13630.
- [15] Agarwal T., Sievert A.C., Komini Babu S. Enhancing durability of polymer electrolyte membrane using cation size selective agents. *Journal of Power Sources*, 2023, **580**, P. 233362.
- [16] Ibrahim A., Hossain O., Chaggar J., Steinberger-Wilckens R., El-Kharouf A. GO-nafion composite membrane development for enabling intermediate temperature operation of polymer electrolyte fuel cell. *International Journal of Hydrogen Energy*, 2020, **45**(8), P. 5526–5534.
- [17] Teixeira F.C., Teixeira A.P.S., Rangel C.M. Chemical stability of new nafion membranes doped with bisphosphonic acids under Fenton oxidative conditions. *International Journal of Hydrogen Energy*, 2023, **48**(96), P. 37489–37499.
- [18] Krasnova A.O., Glebova N.V., Kastsova A.G., Rabchinskii M.K., Nechitailov A.A. Thermal Stabilization of Nafion with Nanocarbon Materials. *Polymers*, 2023, **15**(9), P. 2070.
- [19] Glebova N.V., Mazur A.S., Krasnova A.O., Pleshakov I.V., Nechitailov A.A. Investigation of stability of composite Nafion/nanocarbon material. *Nanosystems: Physics, Chemistry, Mathematics*, 2023, **14**(2), P. 202–207.
- [20] Primachenko O.N., Kulvelis Y.V., Odinokov A.S. New Generation of Compositional Aquivion®-Type Membranes with Nanodiamonds for Hydrogen Fuel Cells: Design and Performance. *Membranes*, 2022, **12**(9), P. 827.
- [21] Kastsova A.G., Krasnova A.O., Glebova N.V., Pelageikina A.O., Nechitailov A.A. Long-term durability of membrane electrode assemblies of proton exchange fuel cells: challenges and solutions. *Russian Chemical Reviews*, 2025, **94**, RCR5135.
- [22] Krasnova A.O., Glebova N.V., Nechitailov A.A., Kastsova A.G., Pelageikina A.O., Kirilenko D.A., Shvidchenko A.V., Shestakov M.S., Koroleva A.V., Khrapova E.K. Comparative Study of Graphite Exfoliation Techniques Using Nafion as a Surfactant. *C-Journal of Carbon Research*, 2025, **11**, P. 76.
- [23] Rambabu G., Bhat S.D., Figueiredo F.M.L. Carbon Nanocomposite Membrane Electrolytes for Direct Methanol Fuel Cells—A Concise Review. *Nanomaterials*, 2019, **9**, P. 1292.
- [24] Method of Producing Porous Carbon Material Based on Highly Disintegrated Graphite, Patent Patent 2014116365/05 Russia: IPC C01B 31/04, Mazin V.I., N 2581382, Bull. N 11, 2016, p. 9.
- [25] Kachala V.V., Khemchyan L.L., Kashin A.S. Target-oriented analysis of gaseous, liquid and solid chemical systems by mass spectrometry, nuclear magnetic resonance spectroscopy and electron microscopy. *Russian Chemical Reviews*, 2013, **82**(7), P. 648–685.
- [26] Tang Q., Li B., Yang D., Ming P., Zhang C., Wang Y. Review of hydrogen crossover through the polymer electrolyte membrane. *International Journal of Hydrogen Energy*, 2021, **46**, P. 22040–22061.
- [27] Lage L.G., Delgado P.G., Kawano Y. Thermal stability and decomposition of nafion® membranes with different cations. *Journal of Thermal Analysis and Calorimetry*, 2004, **75**(2), P. 521–530.
- [28] Komma M., Marth A., Maier M., Hutzler A., Böhm T., Thiele S. Applicability of Graphene Oxide Interlayers in PEMs for Reducing Crossover in Electrochemical Acetone Hydrogenation Reactors. *Journal of The Electrochemical Society*, 2024, **171**, P. 104502.
- [29] Chien H.-C., Tsai L.-D., Huang C.-P., Kang C., Lin J.-N., Chang F.-C. Sulfonated graphene oxide/Nafion composite membranes for high-performance direct methanol fuel cells. *International Journal of Hydrogen Energy*, 2013, **38**, P. 13792–13801.

- [30] Taghiabadi M.M., Zhiani M., Silva V. Effect of MEA activation method on the long-term performance of PEM fuel cell. *Applied Energy*, 2019, **242**, P. 602–611.

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