

From Detection to Substitution: Scientific Challenges of PFAS in Hydrogen Technologies

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Abstract

Per- and polyfluoroalkyl substances (PFAS) are widely used in hydrogen technologies, particularly as perfluorosulfonic acid (PFSA) in proton exchange membrane (PEM) fuel cells and electrolyzers, due to their chemical stability, hydrophobicity, and ion-conducting properties. However, these same properties pose environmental and regulatory challenges, as PFAS are persistent, bioaccumulative, and potentially toxic. This review provides a comprehensive overview of PFAS in the hydrogen sector, examining degradation pathways, emission sources across production, use, and end-of-life stages, and the associated environmental and analytical challenges. Current research highlights the emission of fluoride ions and polymer fragments during device operation, but substantial knowledge gaps remain regarding emissions from manufacturing, recycling, and nanoparticle release. Strategies for mitigating PFAS-related risks, including effluent filtration and alternative fluorine-free membranes and ionomers, are discussed, alongside the technological, chemical, and operational hurdles associated with their implementation. By mapping current scientific understanding and outstanding research needs, this review aims to guide efforts toward environmentally responsible, sustainable hydrogen technologies while reducing reliance on PFAS.

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H₂
HYDROGEN

Introduction

Per- and polyfluoroalkyl substances (PFAS) are a class of synthetic chemicals valued for their chemical and thermal stability, hydrophobicity, and resistance to degradation. These properties make them integral to numerous industrial applications, including hydrogen technologies, where perfluorosulfonic acid (PFSA)—a PFAS subclass—is widely used in polymer electrolyte membranes and electrocatalyst layers for proton exchange membrane (PEM) fuel cells and electrolyzers. However, the very same properties that make PFAS ideal for energy conversion components also raise environmental and regulatory concerns due to their persistence, bioaccumulation potential, and emerging links to adverse health and ecological effects.¹

In recent years, growing scrutiny over PFAS has triggered regulatory developments and intensified scientific inquiry into their lifecycle impacts across technologies.² While some research in the hydrogen sector has focused on degradation pathways and the release of fluoride and fluorinated organic fragments during device operation, PFAS emissions also occur at other lifecycle stages, including production, manufacturing, and end-of-life handling. Furthermore, substantial knowledge gaps remain on the path to fully understand degradation processes and the development of adequate analytical tools—particularly in the context of electrolyzers, upstream emissions, nanoparticle formation, and long-term environmental behaviour. Simultaneously, it is imperative to advance research on filtration technologies aimed at preventing emissions, as well as on the identification and development of alternative materials that can replicate the unique functional properties required for various components within fuel cells and electrolyzers.

This paper provides a comprehensive overview of the current state of research on PFAS in the hydrogen sector. It examines degradation mechanisms and emission profiles, explores sources of PFAS release across the production–use–disposal chain, reviews the environmental and analytical challenges, and surveys emerging mitigation and substitution strategies. By mapping the scientific progress and outstanding research challenges, this review aims to inform ongoing efforts to manage PFAS-related risks and accelerate the development of safe, sustainable hydrogen technologies.



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PFAS
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Current State of Research

Degradation of H2 technologies and link with emissions

Polymer electrolytes in fuel cells and electrolyzers are for the most part relying on perfluorosulfonic acid (PFSA) in both the membrane and electrocatalyst layers. It is highlighted, however, that the PFSA implemented in the membrane and in the electrocatalyst layers have to satisfy different requirements.³ PFSA for membranes must yield a high proton conductivity (to minimize ohmic drops) and a low gas permeability (to maximize durability). On the other hand, PFSA for electrocatalyst layers must exhibit a high gas permeability to facilitate mass transport. PFSA consists of a fluorocarbon-based backbone with perfluoroether side chains terminated by sulfonic acid groups and are classified as polyfluoroalkyl substances (PFAS). The use of PFAS has come under scrutiny due to their exceptionally high stability.⁴ This stability, however, makes them also almost irreplaceable in PEM fuel cells and electrolyzers.

Despite their remarkable stability, it has been known that the degradation of PFSA leads to the emission of fluorine containing compounds early on. In fact, the emission of fluoride ions has been suggested as a metric to monitor fuel cell and electrolyzer membrane degradation in 1990 and used as such ever since.⁵ The underlying degradation mechanism is based on the generation of radicals from hydrogen peroxide, the latter formed either as a byproduct of the electrode processes or from gas crossover. Depending on the site of chemical attack as well as general polymer structure, it has been assumed in the past that the majority of emitted fluorine is in the form of fluoride ions or HF.⁶ However, more recent data shows that besides fluoride ions, substantial amounts of polymer fragments are emitted as well.⁷⁻⁹ A significant amount of data has been collected on fuel cells and, to some extent, electrolyzers operating under conditions that selectively allow for a high level of crossover and in general favour the generation of radicals. Such conditions are achieved under the OCV hold tests proposed by the US Department of Energy.^{10,11} While these degradation pathways only have limited transferability to real applications, where countermeasures are specifically taken to prevent harmful conditions, similar results have been replicated under operation.^{9,12}

Throughout literature, a dependency of the emission of fluorinated species as well as fluoride (and their respective ratios) on time, conditions and materials has been recorded and it is clear that there are underlying influencing factors that need to be carefully considered.^{7,8,13} For example, it was found that an initial chain cleavage can lead to the formation of more degradation-susceptible carbonyl end groups, which allow for consecutive chain unzipping as proposed by Coms et al..⁶

While much research has been dedicated to enhancing the understanding of membrane degradation, it is worth noting that the same or similar compounds are used in the electrocatalyst layers as well. Such PFSA can undergo degradation, which leads to the emission of fluorinated species just the same. The proton-exchange membrane, on the other hand, typically does not only include the proton-conducting ionomer, but also chemical and mechanical stabilisers, with PTFE being one of them. In addition, layers such as the microporous layer, the gas diffusion layer or the porous transport layer are commonly treated with PTFE in order to modulate their hydrophobicity and thus the water management in a fuel cell or in an electrolyser. Processing aids can also contain fluorine. These perfluorinated compounds can degrade as well, contributing to the overall emission of fluorinated compounds ^A.

Sources of emissions during the production, usage and recycling

As of today, research into PFAS emissions in the hydrogen industry has primarily focused on the operation of electrochemical cells—namely fuel cells and electrolyzers. These studies typically examine degradation products released under accelerated aging conditions or stress tests.^{15–17} However, PFAS contamination has also been detected in the environment near chemical industry sites, indicating a broader range of emission sources requiring attention.^{18,19}

The production stage is a critical but underexplored contributor of PFAS emissions. This includes the synthesis of PFSA-based ionomers, membrane fabrication, electrocatalyst ink formulation, and the manufacturing of catalyst-coated membranes (CCMs). Mechanical processes such as the fabrication of membrane-electrode assemblies (MEAs) and the assembly of cell stacks—especially during sealing component integration—can cause abrasions and an unintentional particle release.

Environmental monitoring has revealed elevated PFAS levels around industrial production sites, emphasizing that significant emissions may occur during manufacturing and not only during use.¹⁸ These findings call for a more detailed assessment of upstream PFAS sources in hydrogen technologies.

During operation, PFAS-based materials are subjected to chemical and mechanical stresses. The aggressive electrochemical environment found in fuel cells and electrolyzers can lead to degradation, while pressure fluctuations and flow dynamics may gradually release PFAS into effluent streams.

At end-of-life system disassembly, disposal, or recycling introduces additional risks. Me-

A From conversation notes with Ian T. Cousins, Juliane Glüge and Amanda Rensmo, see also: Dalmijn, Joost; Glüge, Juliane; Scheringer, Martin; Cousins, Ian T. (2024): Emission inventory of PFASs and other fluorinated organic substances for the fluoropolymer production industry in Europe. In *Environmental Science: Processes & Impacts* 26 (2), pp. 269–287. DOI: 10.1039/D3EM00426K.

chemical handling may damage PFAS-containing components, and chemical recycling could release harmful substances if not properly managed. These aspects remain insufficiently studied.

Environmental impact of PFAS and analytical techniques for their detection

The monitoring of fluoride ions – which are detectable by common analytical techniques such as high-performance liquid chromatography and ion chromatography (HPLC/IC) or fluoride ion-selective electrodes (F-ISE) – already poses many challenges. The applicable techniques require substantial volumes of sample, especially if sample preparation (e.g., due to a complex matrix) is needed. In addition, such techniques are time-consuming and equipment-intensive, giving neither the possibility for finely time-resolved monitoring of emissions nor straightforward possibilities for online monitoring.

At the same time, the decomposition of PFSA is known to lead not only to the emission of fluoride ions, which occur naturally in salt form, but also of the much more concerning polymer fragments as shown in recent work by Yandrasits et al.,^{7,8} who use liquid chromatography and mass spectroscopy (LC-MS), IC as well as combustion ion chromatography (CIC) to allow for a more holistic understanding of the degradation products. However, although the detection and identification of some of the fragments obtained upon PFAS and PFSA degradation is progressing, the heterogeneity and low concentrations of such fragments under regular operation remains an unsolved challenge for analytical techniques.

PFAS capture and avoiding emissions

Polymers belonging to the perfluorosulfonic acid (PFSA) subclass of PFAS are widely used as both ion-exchange membranes and electrocatalyst layer ionomers in state-of-the-art proton exchange membrane fuel cells and electrolyzers. In the last decade, the development of fluorine-free aromatic hydrocarbon (AH)-type alternatives to PFSA has been at the centre of significant research interests. Compared to PFSA, AHs often involve trade-offs, notably reduced stability against radical-induced degradation, resulting in a shorter in-device lifespan. Among AH-type materials, sulfonated polyphenylenes are the only ones that exhibit a sufficient chemical stability and performance in comparison with PFSA.^{20,21} However, their use in energy conversion devices remains limited to low TRL. Given that PFSA cannot be replaced by alternative materials in the short- and middle-term, it is crucial to focus on understanding and mitigating emissions into natural water bodies resulting from the chemical-induced degradation of PFSA-based materials.

Various remediation techniques exist, that are based on the separation and/or destruction of PFAS that are already present in natural waters.²² For low PFAS concentrations, typical of natural water bodies, concentration-based methods are often more cost-effective due to the higher energy demand and complex infrastructure (i.e., due to scalability issues) required for destruction-based approaches. Several high-TRL remediation technologies that are based on PFAS concentration are currently being developed to effectively remove PFAS contaminants from various water bodies or landfills, and include: (i) foam fractionation;^{23,24} (ii) filtration over granular activated carbons;²⁵ and (iii) adoption of ion exchange resins.^{26,27} The limited selectivity of these methods often necessitates specific material

compositions or frequent filter regeneration. Recently, an approach comprising a fluorinated anion-exchange membrane-based sorbent achieved a removal efficiency of over 98% for 11 different types of PFAS, demonstrating its potential for advancing to higher TRLs.²⁸

Alternatives to PFSA-based membranes and ionomers and implications of alternative technologies on fuel cell technologies

Over the last decades, numerous fluorine-free proton-exchange membranes have been investigated as alternatives to Nafion for use in fuel cell and electrolyser technologies, including poly(arylene ether ketones),²⁹ poly(arylene ether sulfones),³⁰ polyimides,³¹ poly(arylene sulfone sulfides),³² and poly(phenylenes).²¹

Recent advances in the field of fluorine-free PEMs have led to drastically improved performance and durability of these alternative membranes, with recent reports showing comparable results to PFSA. Qelibari et al. employed a sulfonated poly(phenylene sulfone) (sPPS) membrane in a single-cell proton exchange membrane water electrolyser, demonstrating a performance of 3.2 A/cm² at 1.8 V and stable operation for 650 hours with a degradation rate of 80 μ V/h.³³ Adamski et al.²¹ and Yazili et al.³⁴ employed poly(phenylene) and poly(phenylene sulfone) membranes, respectively, in single-cell PEMFCs, demonstrating a similar performance in comparison to PFSA. These studies also demonstrate an improved durability compared with PFSA under accelerated stress tests consisting of an extended open circuit voltage hold at 90 °C and 30 %RH. A recent study, however, has shown that this accelerated stress test designed for PFSA-based membranes is not appropriate for hydrocarbon-based membranes due to the different degradation mechanisms affecting the latter.³⁵ To definitively prove the durability of non-fluorinated membranes in fuel cell applications, it is imperative that future studies perform extended “in-situ” drive cycles under real operating conditions.

While a steady output of high-quality research investigating alternative fluorine-free PEMs in electrochemical hydrogen technologies has been ongoing since the 1990s, the Clean Hydrogen Joint Undertaking (CH JU) has recently highlighted this area of research as a key topic in the impending uncertainty surrounding the use of PFAS-based materials in Europe. In 2023, the SUSTAINCELL (101101479) and HIGHLANDER (101101346) projects kicked off, where part of the activities will be dedicated to the development of fluorine-free membranes and ionomers. In 2024, the CH JU launched a call dedicated to the development of non-fluorinated components for fuel cells and electrolyzers (HORIZON-JTI-CLEANH2-2024-05-02), where three projects will begin in 2025 : PROMISERS (101192151), FASTCH2ANGE (101192325), and ECOPEM (101192366).

The recent advances in fluorine-free PEM research have led to the commercialization of a few different membranes and ionomers, mainly through Ionomr Innovations (Canada) and Toray (Japan). Additionally, Ionysis (Germany) is focusing on producing membrane electrode assemblies (MEAs) with PFAS-free materials. Many of the largest European polymer manufacturers also have ongoing R&D initiatives to develop fluorine-free membranes and ionomers. Despite the recent flurry of commercial interest in fluorine-free materials, there are currently no commercially available proton exchange membrane fuel cells or electrolyzers which incorporate these alternative materials. This points to the fact that many challenges remain to be overcome and must be addressed through low TRL research.

PFAS & Sealing technologies for H₂ applications

Within the hydrogen value chain, fluoropolymers—such as FKM, FFKM, and PTFE—and fluorinated elastomers (commonly referred to as fluoroelastomers) are currently employed in gaskets and sealing components in most electrolyser and fuel cell types. These materials are also integral to components of hydrogen transport and distribution infrastructure, including regulator membranes, meters, and valves. Their exceptional properties, including high thermal and chemical resistance, non-wetting and non-sticking properties, and low friction coefficients, render them essential for meeting the stringent performance criteria of hydrogen applications. In particular, their use is critical to ensuring high levels of tightness and minimizing fugitive emissions from both static and dynamic sealing systems. Ongoing research has been investigating the behaviour of these polymers under high-pressure hydrogen environments in both static and dynamic sealing contexts.^{36,37}



3



Research Challenges

Degradation of H₂ technologies and link with emissions

To this day, the combination of limited availability of analytical techniques, low concentration and heterogeneity of the degradation products make their identification difficult and in particular limit the possibilities for time-resolved detection and identification as well as online monitoring beyond the emission of fluoride ions. In addition, there is scientific consensus that the underlying degradation mechanisms are not fully and sufficiently understood as the exact interplay between operating conditions and degradation emission products remains unknown. Furthermore, much of the work on the detection and identification of PFSA degradation products has been conducted based on fuel cells, with far less information available for electrolyzers.

Sources of emissions during the production, usage and recycling

There is a significant knowledge gap regarding the nature, quantity, and environmental impact of PFAS emissions as well as their relation to fluoride emissions across all lifecycle stages of hydrogen technologies. While fluoride ions and polymer fragments are known degradation products in the use phase, much less is understood about emissions during production and recycling. Particularly concerning are bioavailable compounds for which data is scarce, despite their potential ecological and toxicological relevance.

Analytical challenges further complicate the issue. Many PFAS compounds occur at trace levels, within complex matrices, or as nanoparticles—forms that current methods struggle to detect reliably. This limits our ability to characterize emissions and assess their associated risks.

To address these challenges, future research should focus on closing key knowledge gaps by generating robust data, enhancing analytical methods, and investigating emission pathways and material behaviour. At the same time, mitigation strategies—such as filtration, material recovery, and cleaner production and recycling processes—must be developed and validated. The overarching goal is to understand and reduce PFAS-related risks, enabling the environmentally responsible use of hydrogen technologies.

Environmental impact of PFAS and analytical techniques for their detection

The OECD identified more than 4 700 individual PFAS-related CAS numbers, referring to compounds in commercial use and often with an unknown impact on the environment

and human health, but often also with little to no alternative.^{38–40} To add to the complexity, there are also limited means to detect these compounds individually, as standards are missing and non-targeted approaches for detection are time consuming. In comparison studies between the extractable organic fluorine and known, selected fluorinated organic compounds, in some cases only 10% of species could be identified, highlighting the limited possibilities in analytics available today.^{41,42} An additional challenge lies in the fact that emissions are not only in the form of broken-down polymer fragments in liquid or gaseous phase, but also in the form of highly bioavailable nanoparticles (K. Schreyer, “Conversation notes Kristin Schreyer and Jörg Feldmann (University of Graz).” 2024). Currently, there are no techniques able to detect these particles and their potential emission from fuel cells and electrolyzers is unexplored.

PFAS capture and avoiding emissions

PFAS capture is challenging due to several factors summarized below.⁴³ The high stability of carbon-fluorine bonds makes PFAS highly resistant to destruction-based approaches and poses challenges for long-term waste management in methods that focus on PFAS concentration. PFAS include thousands of compounds with varying chain lengths and chemical structure (e.g., functional groups), complicating the development of uniform removal strategies. PFAS are often present at extremely low concentrations, i.e., ppt levels, requiring highly efficient removal technologies complemented by highly sensitive analytical techniques for detection. Standard water treatment methods (e.g., coagulation and flocculation) are ineffective at these concentrations. Most high-TRL approaches face challenges with capture efficiency, as PFAS compounds of different chain lengths exhibit significantly different mobility and adsorption behaviour. Moreover, the presence of other inorganic or organic contaminants aggravates the selectivity issue and necessitates frequent adsorbent regeneration (or replacement), resulting in increased operational costs. PFAS-selective sorbents show a high selectivity; however, they contain fluorinated constituents, which are necessary for halogen-bonding interactions with the target compounds. Moreover, evolving regulations make it difficult to select optimal long-term solutions, requiring constant adaptation of existing technologies.

Effluent filtration of energy conversion devices may address several of the challenges outlined above: it enables targeted removal of PFAS directly at the source, before its discharge into the environment and its subsequent dilution. Moreover, the effluent typically contains higher concentrations of target contaminants and lower concentrations of background contaminants compared to natural waters, making the removal process more effective and selective.

The use of PFAS-selective sorbents in effluent filtration provides a more targeted and efficient approach for PFAS removal, demonstrating promising potential as a long-term solution for PFAS remediation.⁴⁴ However, challenges related to filter durability, cost, and the management of concentrated PFAS waste must be addressed to advance the TRL of this approach. The latter issue might be alleviated for instance by combining filtration with already existing high TRL destruction-based approaches.

Alternatives to PFSA-based membranes and ionomers

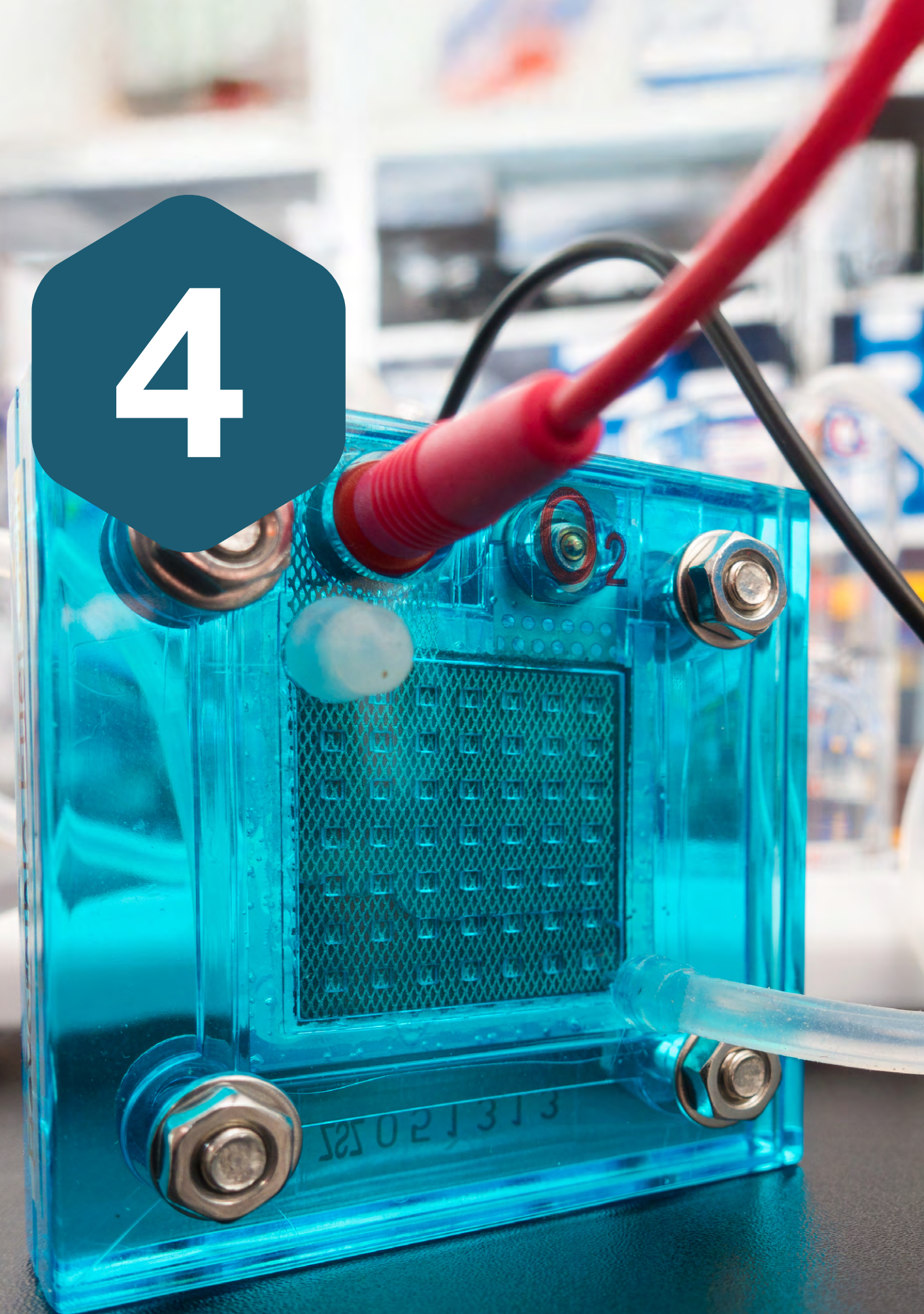
One of the main considerations for the development of non-fluorinated ionomers is that the sulfonic acid groups tethered to a hydrocarbon backbone do not exhibit the same super-acidity of those tethered to a perfluorinated backbone. Consequently, non-fluorinated ionomers require a much higher density of sulfonic acid groups (i.e., higher ion exchange capacities – IECs) to achieve similar proton conductivities as PFSA ionomers. The high density of sulfonic acid groups, however, also leads to increased water absorption by the membrane and electrocatalyst layer ionomers, resulting in excessive swelling and a reduced mechanical stability. The lack of proven stability has been a major challenge in the area of non-fluorinated ionomer development. Additionally, the incorporation of fluorine-free ionomer binders in the electrocatalyst layer is a significant challenge due to unmitigated swelling, low gas permeability, potential electrocatalyst poisoning/deactivation through interactions with the phenyl groups, and the potential for electrochemical oxidation of phenyl groups at elevated potentials in electrolyser applications.

These new materials will also require re-thinking some of the approaches to fuel cell and electrolyser state-of-health monitoring, as well as degradation mitigation strategies.

PFAS & Sealing technologies for H₂ applications

Despite the progresses made so far significant research gaps remain, particularly concerning the development of per- and polyfluoroalkyl substances (PFAS)-free alternatives. Further research and development are needed to design and evaluate new sealing materials and configurations that can meet or exceed current in-service performance specifications. This includes the establishment of dedicated characterization methods and testing platforms to accurately assess material behaviour under operational conditions. Prioritizing the development of sustainable, high-performance alternatives to PFAS-based materials is essential to ensure safety, reliability, and environmental compliance in both static and dynamic hydrogen sealing applications.

4



Timeline and Resources

Degradation of H₂ technologies and link with emissions

Research regarding the better linkage between material selection, operating conditions and the emission of fluorinated species is already underway. However, due to the complexity of the topic and the multitude of influencing factors, it is evident that it will not be possible to answer the linked research questions in the short term. With growing means for analysis, identification and quantification of fluorinated species, the mechanistic understanding of the underlying degradation mechanisms is expected to improve. Furthermore, the in-depth understanding of the harmful conditions is also expected to accelerate the integration of novel, non-fluorinated ionomers.

Sources of emissions during the production, usage and recycling

Establishing a comprehensive understanding of PFAS emissions across the entire life-cycle of hydrogen technologies is a long-term objective. This effort is challenged by the complexity and cost of sampling and analytical techniques, particularly when dealing with trace concentrations and diverse PFAS compounds. However, certain aspects require immediate attention: in particular, emissions from systems during operation should be assessed as soon as possible. Early monitoring capabilities would allow for the identification of critical emission pathways and enable retrofitting or mitigation measures in existing systems where necessary.

In the short to medium term, focused studies on emissions during recycling and dismantling processes are also essential. These areas remain underexplored but are increasingly relevant as more systems approach end-of-life. Without proper understanding and controls, there is a risk that such systems could contribute to significant environmental harm.

Environmental impact and analytical techniques

It is evident that the development of analytical techniques and reliable test procedures is mandatory in order to fully understand the emission pathways and the potential environmental risks. This is a concern that reaches far beyond hydrogen technologies, but also impacts them directly. A close exchange between different fields and the early validation of novel analytical techniques for their suitability for hydrogen technologies is crucial for a fast adoption.

PFAS capture and avoiding emissions

There is a significant increase in the use of proton exchange membrane (PEM) electrolyzers and fuel cells, driven by the global shift towards clean energy, hydrogen production and use. In the absence of high-TRL alternative materials to PFSA-type polymers, their capture needs to be addressed in the medium term. Low-TRL solutions already exist that can be further developed.

Alternatives to PFSA-based membranes and ionomers

With the recent support of the CH JU, at least five European projects focused on the development of fluorine-free membranes and ionomers will be complete before 2030, potentially providing promising materials demonstrated up to TRL 4. Any materials developed within this period, however, must undergo an extensive qualification and demonstration period in operational fuel cell and electrolyser stacks run in realistic conditions. Concerted efforts between industry and research partners will be required to bring low TRL research developments through to market-ready solutions in a timely manner. In parallel, it is imperative that low TRL research continues to be funded to ensure innovation does not remain stagnant in favour of only upscaling the most promising state-of-the-art solutions.



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