

Perfluoroalkyl decorated cerium oxide nanoparticles as compatible radical scavengers in Aquivion®-based proton exchange membrane fuel cells with improved durability

Diego Stucchi^{a,*}, Alessandro R. Ferrari^a, Tommaso Caielli^a, Antonio G. Di Tolla^a, Rodrigo Schneider^b, Marc Dupont^b, Daniele Mora^c, Elena Colomo^c, Gioele Pagot^d, Vito Di Noto^d, Andrea Baricci^c, Sara Cavaliere^b, Piercarlo Mustarelli^{a,**}

^a Department of Materials Science, University of Milano-Bicocca, Milan, Italy

^b ICGM, Université de Montpellier, CNRS, Montpellier, France

^c Department of Energy, Polytechnic University of Milan, Milan, Italy

^d Section of Chemistry for the Technology (ChemTech), Department of Industrial Engineering, University of Padua, Italy

ARTICLE INFO

Keywords:

Fuel cells
Proton exchange membranes
Aquivion®
Radical scavengers
Cerium oxide
Nanoparticles decoration
Fluoroalkyl silanes

ABSTRACT

Proton exchange membrane fuel cells (PEMFCs) are highly efficient devices for converting chemical energy into electrical energy. At present, however, their large-scale implementation is primarily hindered by the limited lifetime of the membrane electrode assembly (MEA), which typically utilizes perfluorinated ionomers, such as Nafion™. Current research focuses on incorporating radical scavenging species into the MEA to enhance durability. This work investigates the use of functionalized CeO₂ nanoparticles coupled with Aquivion®, a short-side-chain ionomer that outperforms state-of-the-art Nafion™. The novelty lies in the application of organosilanes bearing fluorinated chains as grafting agents on the CeO₂ surface to improve filler-polymer compatibility. The most promising nanocomposites exhibit uniform filler dispersion, and a 50% reduction in both swelling ratio and *ex-situ* fluoride ions emission rate, while maintaining conductivity values above 150 mS cm⁻¹ at 80 °C and 100% RH. Furthermore, fuel cell performance comparable to, or exceeding, pristine Aquivion® was observed, with negligible degradation after >650 h of accelerated stress testing. These findings could pave the way for a new generation of composite membranes featuring polymer-tailored scavenger functionalization.

1. Introduction

Despite the significant benefits offered by fuel cells as a method to fulfil the world's demand for energy in a non-polluting cyclic way, the technology is still being commercialized only in niche markets. Nonetheless the hype on this remains strong as the U.S. Department of Energy has set some achievable targets for proton exchange membranes fuel cells (PEMFCs) [1], and the European Union founded many research activities on the matter, through the new Green Deal, to reduce the gap with current more impacting technologies [2]. These include a reduction in costs, improvement in performance, and an increase in operational lifetime. To properly tackle the first issue, extensive studies have been made regarding platinum group metal (PGM)-free catalyst that maintain high efficiency greatly reducing the costs [3,4]. At the same time, new

ionomers, like Aquivion®, have been commercialized. These possess short lateral side chains (SSC), compared to Nafion™'s long side chains (LSC), and show promising results performance-wise [5,6]. Lastly, the degradation is both of the catalyst layers [7,8] and of the membrane [9,10]. Due to the underlying complex mechanisms, this is often regarded as one of the crucial issues hindering a wider spreading of PEMFCs.

Polymer degradation occurs through both mechanical and chemical mechanisms. The former is caused by the combined effect of the compressive stresses applied to the membrane electrode assembly (MEA) within the fuel cell stack, and the membrane's dimensional changes caused by its swelling and shrinking during operational cycles [11,12]. Many strategies have been pursued to improve the mechanical resistance of PEMs, ranging from thermal treatments [13,14] to the preparation of composite membranes, either with polymeric

* Corresponding author.

** Corresponding author.

E-mail addresses: diego.stucchi@unimib.it (D. Stucchi), piercarlo.mustarelli@unimib.it (P. Mustarelli).

<https://doi.org/10.1016/j.ijhydene.2026.158193>

Received 30 June 2026; Received in revised form 12 October 2026; Accepted 16 October 2026

Available online 20 October 2026

0360-3199/© 2026 The Authors. Published by Elsevier Ltd on behalf of Hydrogen Energy Publications LLC. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

reinforcements [15] or with inorganic fillers [16].

Arguably more impactful on the loss of lifetime of PEMFC, is the chemical degradation of the polymer [17], which may be caused by different radical species [18]. To prevent the disruptive interaction between these radicals and the polymer, the implementation of scavenging fillers into PEMs has been studied extensively [19,20]. The use of organic radical scavengers [21], metal ions [22,23], oxides [24] and other complexes has been proposed [25,26]. The most promising solution seems to be, by far, the use of cerium, either as an oxide or as ions, due to its interconversion between Ce(III) and Ce(IV) upon reaction with different species present in a fuel cell environment [27–30]. It was proved that Ce ions tend to migrate under operation conditions [31], which causes a loss in their performance as scavengers [32] and issues in the catalyst layer [33]. For this reason, although attempts were made to block the ions motion [34,35], research focused on the use of CeO₂, mostly in the form of nanoparticles [36–39]. State-of-the-art solutions revolve around the use of SSC polymers coupled with immobilized cerium oxide nanoparticles [40–43] that may be grafted to improve their adhesion and compatibility with the polymer matrix, [44,45], or modified to increase their scavenging ability [46].

The goal of this work is to build upon this idea while adopting a complementary, yet contrasting, approach: in place of a coating that is hydrophilic [44] or straight up charged [45], we want to make the CeO₂ nanoparticles (NPs) chemically compatible with the Aquivion® backbone, by means of a proper functionalization with fluorine-containing pendants. This is expected to have multiple benefits in the final nanocomposite membrane. On one hand, it may facilitate the NPs dispersion within the polymer matrix. Secondly, we assume that the decorated NPs will be integrated into the hydrophobic domain of the membrane. This should result in less disruption to the interconnection of ionic channels, which is the primary factor ensuring efficient proton conductivity. Possible additional benefits may come in the form of an anchoring effect of the nanoparticles, thus impeding their motion, reducing potential clustering overtime, and limiting dissolution of the oxide which, in turn, causes Ce ions leaching and the loss of the scavenging effect. At the same time, the functionalization should not cover the whole surface of the cerium oxide since this would prevent the interaction between the radical species and the Ce (III) and Ce (IV) sites, thus lowering the filler's scavenging efficacy.

We have investigated five different (organo)silanes as grafting agents for CeO₂ NPs. Aminopropyl triethoxy silane is widely employed in the decoration of many oxides, especially SiO₂ [47], and it has been used as a baseline to investigate whether any changes in the membrane's properties were caused by the NPs' functionalization with moieties resembling the polymer, or merely by the presence of *any* grafting agent on them. The other four silanes all bear some fluorinated moiety as a lateral chain of increasing length, and thus similarity, to Aquivion®'s backbone. We prepared seven membranes, including pure Aquivion® used as a reference, a sample with non-decorated cerium oxide nanoparticles and five nanocomposite PEMs containing the five grafted NPs. These samples were characterized as far as their physical-chemical and functional properties are concerned, showing promising results in terms of lifetime improvement without significant performance losses. Their performances and durability in a PEMFC device were also investigated proving encouraging with a meaningful lifetime extension under accelerated stress test (AST) conditions when compared to the bare polymer, while retaining comparable performance to the reference material.

2. Experimental section

2.1. Starting materials

Solvay Specialty Polymers (now Syensqo) supplied Aquivion® dispersion (D72-25BS). CeO₂ nanoparticles (<25 nm particle size by Brunauer-Emmett-Teller, BET, analysis of N₂ absorption/desorption

isotherms), KOH pellet (85%), sulfuric acid (95–97%), hydrogen peroxide (H₂O₂ 29–32% wt/wt aqueous solution) and ammonium hydroxide (NH₄OH aqueous solution, 28–30% NH₃ basis) were purchased from Sigma Aldrich. (3-aminopropyl)triethoxysilane (APTES 98%), fluorotriethoxysilane (FETOS, 95%) and toluene (99%) were bought from Alfa Aesar. (3,3,3-trifluoropropyl)trimethoxysilane (3FPTMeOS 95%) and 1H,1H,2H,2H-perfluorodecyltriethoxysilane (PF10EtOS) were purchased from Fluorochem, while triethoxy-1H,1H,2H,2H-tridecafluorooctylsilane (PF8EtOS, 97%) was bought from TCI chemicals. Absolute ethanol and acetone were from Carlo Erba reagents. Lastly, 1-propanol (99+ %), dimethylsulfoxide (DMSO₂) and the total ionic strength adjustment buffer (TISAB III concentrate with CDTA) were purchased from Thermo Scientific.

2.2. Surface grafting procedure

The decoration of CeO₂ was performed as follows: the pristine NPs were dried overnight at 100 °C under vacuum and moved into an argon glove box, where they were placed in a round bottom flask containing toluene. To that is added the desired silane, in a stoichiometry of 1:2 with the CeO₂ hydroxyl groups, derived from TGA, to have a slight excess compared to the theoretical 1:3 ratio. Lastly, NH₄OH was added as a catalyst for the hydrolysis step, and the sealed flask was moved to an already N₂-purged Schlenk line. The reaction environment was purged again with three successive nitrogen-vacuum flushing, then temperature was set to the boiling point of toluene, and the reaction was carried out for 24h in reflux conditions under mild magnetic stirring. To terminate the reaction, the content of the flask was centrifuged at 9000 rpm for 15 min to precipitate the grafted oxide, which was then washed and centrifuged twice with absolute ethanol and twice with acetone to remove any residual toluene and un-reacted silane or catalyst. Finally, the functionalized NPs were dried in vacuum at 50 °C overnight and stored for further use. A scheme of reaction is reported in Fig. 1. The resulting functionalized NPs were labelled according to the functional group of the sidechain of the silane that was grafted on their surface, as clarified by Fig. 1.

2.3. Membrane preparation

For the specific system under investigation a CeO₂ loading of 2–3% of the Aquivion® weight is regarded as the one that maximizes the conductivity of the composite [45,48,49]. In this work, however, we aimed at a 5% loading, in accordance to previous literature [50], to emphasize the effect of the filler. A specific procedure was performed to obtain a homogeneous mixture of Aquivion®, water, 1-propanol, DMSO₂ and CeO₂ NPs in the following percentages:

We highlight that the commercially available dispersion of Aquivion® is composed of 25% polymer and 75% water, so it needs to be concentrated to achieve the desired ratio for the procedure reported in Table 1. Also, the amount of added filler is referred to the whole NPs, in case of functionalized ones, not only the cerium oxide core; anyway, the difference is less than 10% of the NPs weight, so accounting for 0.5% of the total membrane weight. To ease the de-glomeration and form a uniform dispersion, each of the five different functionalized NPs, as well as the pristine CeO₂, were ultrasonicated for 10 min in 1-propanol prior to the addition into the concentrated polymer solution. Lastly, a reference membrane without filler was made following the same procedure without the addition of any filler. The membranes were manufactured following two different protocols, depending on characterization they were supposed to undergo. For conductivity, mechanical analysis and cell tests, the dispersion was deposited with Doctor Blade on glass support. All the other characterizations were conducted on films obtained via solvent casting evaporation from glass petri dishes. In both cases, the drying procedure was as follows: 1h at 60 °C, 1 h at 90 °C and an annealing of 30 min at 190 °C. After the annealing, the membranes were left to cool down and detached from the glass support with the help of

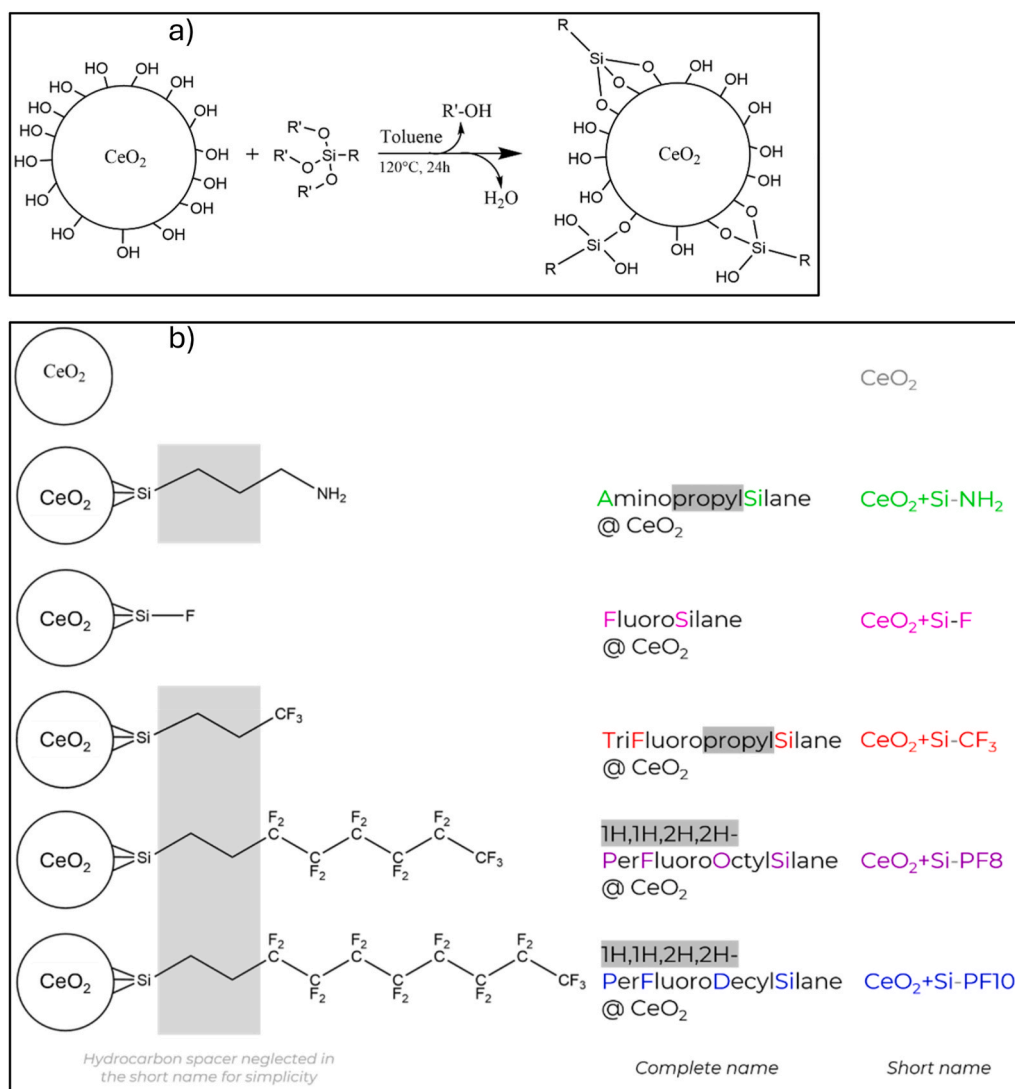


Fig. 1. a) schematic representation of the surface grafting of cerium oxide with organosilanes. b) representation of the resulting decorated NPs, with the extensive nomenclature and the shortened one used in the text.

Table 1

Final percentages (in wt/wt) of all the components of the dispersion, prior to the polymer's casting procedure.

Substance	Amount [%]
Aquivion®	19.8
Water	50
1-Propanol	24.8
DMSO2	4.5
NPs	1

Table 2

Samples investigated and their shortened name, used hence forward for simplicity.

Sample	Short name
Aquivion®	Aq
Aquivion®+CeO ₂	Aq + CeO ₂
Aquivion®+CeO ₂ -NH ₂	Aq + NH ₂
Aquivion®+CeO ₂ -SiF	Aq + F
Aquivion®+CeO ₂ -CF ₃	Aq + CF ₃
Aquivion®+CeO ₂ -PF8	Aq + PF8
Aquivion®+CeO ₂ -PF10	Aq + PF10

Milli-Q® water, re-hydrated in water for 1 day, carefully spread out, dried overnight at 80 °C between weighing papers, and stored for characterization. Following this procedure, seven membranes were obtained (Table 2): a pure Aquivion® one for reference and six nanocomposite films, five of which contain decorated NPs, with four of them being fluorinated on the surface. They were labelled as shown in for simplicity.

For *in situ* AST measurements larger sheets of membranes were produced directly at Syensqo as described in the SI.

2.4. Characterization techniques

2.4.1. Isothermal gas absorption

Brunauer–Emmett–Teller (BET) analysis was conducted using a Quantachrome® autosorb iQ ASiQwin™ instrument with nitrogen as the adsorbate gas at 77 K. Prior to analysis, the pristine CeO₂ nanopowder was degassed at 300 °C (heating rate 5 °C min⁻¹) for 24 h to eliminate moisture and adsorbed gases. The goal was to measure the surface area, and from that the particle's diameter was deduced and compared to XRD-derived crystallite size and the product specification

sheet for the particle's diameter.

2.4.2. Thermogravimetric analysis (TGA)

TGA was performed with a Mettler Toledo TGA/DSC Star® instrument, and the thermogram were analyzed using SraRE® software. The method used consisted of an initial heating from 30 °C to 150 °C with a 10 °C min⁻¹ heating rate, followed by a 10-min isotherm at 150 °C to remove any water that may be bound to the sample, and then of a second heating up to 800 °C with the same 10 °C min⁻¹ rate as before; everything under a 50 mL min⁻¹ air flow. The analysis was performed on pristine and pre-treated CeO₂ NPs to assess the amount of hydroxyl groups on the surface. The amount of silane decorating the surface of the nanoparticles was also estimated with TGA. Lastly, the quantity of ceramic fillers in the nanocomposite membranes was evaluated as the residual weight at 800 °C.

2.4.3. FT infrared spectroscopy in attenuated total reflectance configuration (ATR-FTIR)

FTIR was performed in ATR conditions with a Thermo Fisher Scientific Nicolet™ iS20 instrument and the spectra were analyzed with Omnic™ software. The measurements were performed from 500 cm⁻¹ to 4000 cm⁻¹, with 2 cm⁻¹ resolution and 64 scans, on pristine and decorated CeO₂ nanoparticles to prove the successful grafting of their surface with the desired silane. As a further comparison, the spectra of the silane precursors were recorded and compared to the functionalized nanoparticles highlighting the matching of the fingerprint region.

2.4.4. X-ray diffraction (XRD)

XRD measurements were performed using a Rigaku Miniflex 600 diffractometer equipped with copper K α source and a powder sample holder. The analysis was carried out with Rigaku PDXL2 software. The measurements were performed from 10° to 80° with 10° min⁻¹ rate and 0.02° step. The goal of the analysis was to prove that the CeO₂ crystalline structure of the pristine NPs was maintained after the pre-treatment and to estimate the crystallites size through Debye-Scherrer (Equation S1).

2.4.5. X-rays photoelectron spectroscopy (XPS)

XPS measurements were conducted employing an EnviroESCA spectrometer (Specs) featuring an AlK α X-ray source ($h\nu = 1486.6$ eV). The measurements were carried out under vacuum conditions at 10⁻⁶ mbar. High-resolution spectra were obtained with a pass energy of 40 eV, integrating for 0.1 s step⁻¹, and recording data points at intervals of 0.1 eV step⁻¹. To address experimental errors stemming from charge accumulation, spectra were shifted in binding energy (BE). A BE value of 284.8 eV was applied to correct for the adventitious carbon [51]. Subsequent analysis involved decomposition of XPS curves utilizing the Keystone™ software (Specs) and adopting a Shirley-type background [52]. Quantification parameters were supplied by Specs.

2.4.6. Differential scanning calorimetry (DSC)

DSC characterization was performed with a Netzsch DSC 300 Caliris® Classic, under 20 mL min⁻¹ of argon in the chamber during the measurement. The heating cycle applied is as follows: a first heating from 40 °C to 300 °C with a 10 °C min⁻¹ rate followed by a 5-min isotherm at 300 °C, a cooling step back to 40 °C with a 10 °C min⁻¹ rate, another 5 min isotherm at that temperature, and a second heating up to 300 °C always at the same rate. This second heating is the one reported in the Supplementary Information. The data was analyzed with Proteus software.

2.4.7. Scanning electron microscopy (SEM)

SEM images of the membrane's surface, and cross section, were obtained using an SEM-FEG Gemini 500 Zeiss microscope, with a voltage of 10 kV on graphite sputtered samples. A Bruker QuantaX-Ray detector was used for Energy Dispersive X-ray Analysis (EDX) on the same samples.

2.4.8. Mechanical analysis

The mechanical characterization of the sample was conducted by means of stress-strain experiments, using a Zwick Roell tensile tester, equipped with a maximum charge of 150 N and setting the security maximum charge at 120 N. The samples were cut around 4 cm $\times$ 0.5 cm with a thickness between 10 μ m and 20 μ m. The chamber was set at 25 °C 30% RH and 10 min of conditioning were imposed prior to testing. The tensile speed was 10 mm min⁻¹ and three replicas were measured for each sample.

2.4.9. Water uptake (WU) and swelling ratio (SR)

The membrane's response to being soaked in water was studied in the form of both water uptake and linear swelling ratio. For the assessment of the former, four pieces of each of the seven samples, roughly 100 mg each, were dried overnight in a vacuum oven at 80 °C and rapidly weighed in the dry state. The four pieces were then immersed in 20 mL of water, each in a tightly sealed glass vial, and placed at four different temperatures: 25 °C, 40 °C, 60 °C and 80 °C. After 24 h they were removed from the water, absorbent paper was used to carefully blot the samples to remove any water from their surface, and they were rapidly weighed again in their wet state. WU values were derived from Equation S2.

SR was measured as the difference in length between dry value and wet value. The overall procedure was identical to the one presented above for WU, the only difference being the sample's pieces which are in a precise rectangular shape with sizes ranging around 1 cm $\times$ 5 cm in the dry state. Equation S3 is used to determine SR as a percentage value.

2.4.10. Conductivity measurements

4-electrodes in-plane proton conductivity was measured with a Bekktch BT710 cell on membrane strips of roughly 0.5 cm in width, 3 cm in length and 20 μ m in thickness. The dimensions were measured on the samples after they were left in DI water overnight at room temperature. The cell was fitted in a 740 Membrane Test System (Scribner Ass, NC, USA) that provided the heating-drying-humidifying-cooling down ramp, reported in the SI, through the MTS4 software. The cell was connected to a 4200 Keithley instrument, controlled with LabVIEW™, that scanned from -0.1 V to +0.1 V vs OCV with a 0.02 V steps every 2 s. The current values were recorded. The resistance was extrapolated from the slope of the line and its value, in the most stable region of each segment of the ramp, was used to calculate the material's conductivity from its geometrical factor.

2.4.11. Fenton test

Fenton test was performed to evaluate the degradation of the polymer in presence of radicals. A Fe (II) solution was prepared dissolving 35.5 mg of FeSO₄·7H₂O in 100 mL of H₂O. 10 mL of it were then placed into a Falcon™ tube containing a known weight of dry membrane sample, roughly 50 mg each; to that were added 50 μ L of 0.5 M sulfuric acid aqueous solution and 10 mL of H₂O₂. The Falcon™ was then heated to 80 °C for 4 h, after that the polymer was removed from the tube, and the solution was cooled to room temperature. 10 mL of Fenton solution were mixed with 10 mL of TISAB III and the fluoride concentration was measured using a Thermo Scientific Orion™ fluoride selective electrode in conjunction with an Xs 80⁺ series pH-meter, after the appropriate calibration with 1-10-100 ppm standards from Thermo Scientific. The measured value of mg of fluoride is normalized over the mass of membrane that was degraded.

2.4.12. Fuel cell performance and durability

For each sample a strip of 1 cm $\times$ 3 cm was turned into a catalyst-coated membrane (CCM) through the hot pressing of 0.3 mg cm⁻² Pt/C catalyst layers fabricated by Syensqo at 20 bar for 5 min. This resulted in a 2 cm² active area MEA that was mounted in a differential cell [53], where the samples were conditioned and then characterized. Conditioning protocol was carried out in H₂/air consistently with previous

works [54] at 80 °C under fully humidified conditions with the voltage being changed between 0.6 V and 0.2 V for 15 times for each cycle. A total of 5 cycles were carried out. Performance was assessed through polarization curves in H₂/air with 8/20 stoichiometry and under pressurized conditions (2.3 and 2.5 bar of backpressure at cathode and anode side, respectively). The measurements were performed at 80 °C in 60% and 100% RH. The polarization curve was obtained by scanning every 0.05 V from 0.95 V to 0.4 V, vs. SHE, and holding each step for 3 min (the steps from 0.95 V to 0.85 V were held for 60 s and only in samples whose OCV allowed it).

The in-situ AST was performed with a Greenlight Innovation G1001 test station recording the OCV with the potentiostat embedded in the station. The measurement was conducted following DoE protocol conditions: the cell was kept at 90 °C in OCV conditions 30%RH with 0.5 bar gauge of backpressure at both anodic and cathodic sides, flowing H₂ and air respectively with a rate of 0.250 NLPM for each sample loaded in the stack. Hydrogen crossover was checked once a week. More in detail, two MEAs were assembled using Pt/C carbon-paper GDEs (40% wt Pt, 0.5 mg cm⁻² Pt load catalyst) and membranes fabricated as discussed in SI. This method was chosen to maximize the degradation of the polymeric membrane, rather than trying to mimic as closely as possible real operative conditions of a fuel cell [55,56]. H₂ crossover was measured by flowing nitrogen at the “cathodic” side of the cell and enforcing 0.4 V of potential while measuring the resulting current. Failure conditions were set as OCV dropping below 0.7 V or crossover current above 15 mA cm⁻².

2.4.13. In-plane cerium migration

The goal of the measurement was to simulate the in-plane redistribution of cerium, known to occur in commercial MEAs containing Ce-based radical scavengers [57,58], through an *ex-situ* tailored protocol based on hydrogen pumping operation [59,60] described by Verducci et al. [61]. More in detail, two strips of 2 mm × 1 cm of Pt/C carbon-paper supported GDEs, were hot pressed on opposite sides of a 1 cm × 3 cm sample, applying 20 bar of pressure for 5 min. The MEA was then mounted on a zero-gradient single-cell, in between gaskets providing the correct compression and avoiding gas leakages. The hydrogen pumping measurement was performed, after an overnight conditioning at room temperature under 0.1 NL min H₂ flow, applying a potential difference of 0.5 V between the two electrodes for 15 h at 80 °C, 100% RH and atmospheric pressure under a constant 0.3 NL min⁻¹ flow of hydrogen. To prevent Ce back-diffusion, the membrane was cooled down and dried out in the cell under 1 NL min⁻¹ flow of dry nitrogen. The cerium concentration profile was measured through XRF analysis performed as previously described [61].

3. Results and discussion

3.1. Chemical-physical characterization of the nanoparticles

Initially, the commercial materials were characterized to verify that their properties were consistent with those reported by the supplier. BET analysis (Fig. S1) was employed to evaluate surface area and porosity. The resulting adsorption isotherms and pore size distribution confirmed the non-porous nature of the material. Consequently, the average particle diameter was calculated as 17.3 nm using Equation S4. This result was corroborated by XRD analysis (Fig. S2), where the crystalline domain size was determined to be 17 nm via the Scherrer equation (Equation S1). The close agreement between these values suggests that each nanoparticle can be considered a single crystal. Furthermore, XRD patterns confirmed that the CeO₂ cubic structure was maintained both in the pristine state and after functionalization.

Thermogravimetric analysis (TGA) was performed on the pristine CeO₂ nanoparticles to quantify the surface hydroxyl groups per gram of material, according to Equation S5 [62]. This value served to determine the theoretical amount of silane required to saturate all available surface

hydroxyl sites. The actual quantity of grafted silane was subsequently calculated from TGA data using Equation S6 [63]. From these values, the grafting percentage was derived (Equation S7), while the surface coverage (S.C.) was calculated by incorporating the BET surface area, as described in Equation S8.

Fig. 2 presents the TGA thermograms for pristine CeO₂ and the functionalized NPs. Below the 150 °C isotherm, all samples exhibited minor weight losses (less than 0.2%) attributed to adsorbed moisture. Consequently, the 100% weight reference was normalized at the end of the 10-min isotherm at this temperature (see Section 2.4.2). A stability region is observed up to 200 °C, followed by the thermal degradation of the silane moieties, which concludes around 500 °C. In contrast, pure CeO₂ shows a gradual, asymptotic decrease up to 800 °C. As expected, the highest grafting density was achieved by the silane with the shortest side chain (FETOS, sample CeO₂-SiF), likely due to its minimal steric hindrance (Table 3). Interestingly, APTES reached a grafting percentage three times higher than PF₃MeOS, despite their comparable chain lengths. This disparity may be explained by the terminal amine group of APTES, which is smaller and polar, thereby facilitating the grafting process. As stated, given its established efficiency for oxide functionalization, APTES was selected as a control group. Conversely, the fluoroalkyl silanes showed the lowest functionalization levels (approximately 15% for the shortest and 10% for the two longer chains). This trend confirms that longer chains increase steric hindrance. However, a lower functionalization degree may be advantageous, as it preserves a larger active oxide surface for radical scavenging, as demonstrated by the Fenton test results.

To confirm the efficacy of the functionalization, the grafted nanoparticles were characterized via ATR-FTIR spectroscopy (Fig. S3). Successful grafting was evidenced by the disappearance of the ethoxy group signals and the consistent match between the fingerprint regions of the silane precursor and the decorated nanoparticles.

3.2. Chemical-physical characterization of the membranes

TGA (Fig. S4) allowed to determine the actual loading of inorganic filler within the polymeric matrix, calculated by means of Equation S9. The filler loadings are reported in Table 4. TGA also demonstrated that the thermal stability of the material is not modified by the addition of the scavenger.

Additional information on the thermal response of the materials was obtained via DSC investigation, highlighting a negligible crystalline

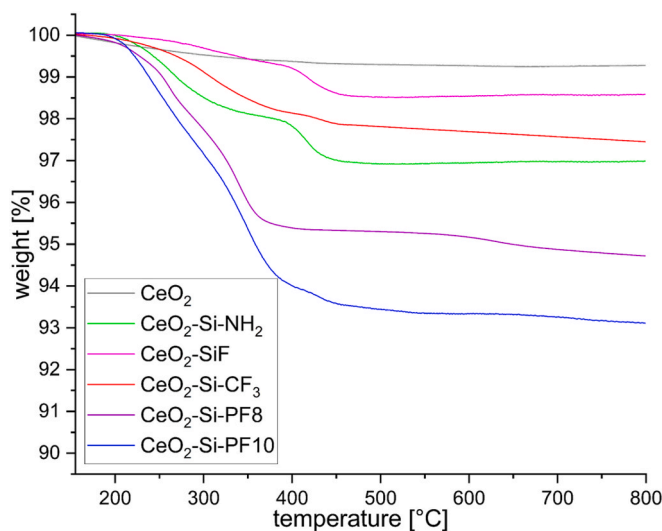


Fig. 2. TGA curves of decorated and pristine cerium oxide nanoparticles, between 150 °C and 800 °C, heating rate 10 °C min⁻¹, in air. The weight at 150 °C was set to 100% for comparison clarity.

Table 3

The percentage of -OH groups that were condensed with the silane after the decoration procedure, S.C. is the quantity of silanes (or -OH in CeO₂) per square centimeter of NPs surface.

Sample name	grafting [%]	S.C. [m mol cm ⁻²]
CeO ₂	/	213
CeO ₂ -Si-NH ₂	57 ± 8	130
CeO ₂ -SiF	70 ± 9	152
CeO ₂ -Si-CF ₃	17 ± 2	30
CeO ₂ -Si-PF8	11.7 ± 0.2	26
CeO ₂ -Si-PF10	11.6 ± 0.1	34

Table 4

CeO₂ load in the final membranes calculated from TGA via Equation S9. The target value was 5% for all nanocomposite membranes. Y: Young's modulus. ϵ_b : elongation at break. Mechanical data are averaged over three replicas. * Measure performed on a thinner membrane (~10 μ m).

Sample name	CeO ₂ load [%]	Y [MPa]	ϵ_b [mA cm ⁻²]
Aq	0.0	218 ± 31	101 ± 5
Aq + CeO ₂	5.2	246 ± 24	100 ± 19
Aq + NH ₂	6.3	235 ± 24	60 ± 15
Aq + F	3.8	265 ± 6	111 ± 13
Aq + CF ₃	4.5	251 ± 8	96 ± 7
Aq + PF8	4.1	220 ± 23*	63 ± 11*
Aq + PF10	4.9	226 ± 15*	20 ± 6*

content of the polymeric matrix and a 2nd order-like transition in all samples (see Fig. S5), which can be attributed to a partial reordering of the polymer strands upon heating [64]. Direct proof of the simultaneous presence in the nanocomposite membranes of the semi-crystalline polymeric matrix and the highly crystalline CeO₂ filler was obtained through XRD measurements (Fig. S6), showing both the amorphous peaks of the polymer and the highly crystalline features of the NPs.

XPS measurements were performed to investigate the presence of CeO₂ on the membrane's surface, as well as the oxidation state of the different elements. Fig. S7 and S8 showed all the expected signals pertaining to the functional groups of the polymer for all elements: C, F, O and S (see SI discussion). No peaks were observed in the Ce 3d, N 1s and Si 2p spectral regions (Fig. S9), indicating that the surface concentration of these species is below the instrumental detection limit (ca. 0.1 at%). This finding reveals that the filler is absent from the topmost layer of the membranes, falling outside the ~10 nm probing depth of XPS.

Fig. 3 shows the SEM surface morphological images (left), and the corresponding backscattered elemental maps (right) for some selected samples. The morphological images show that all the samples have similar dense microstructure. The elemental maps demonstrate the presence of filler particles in the nanocomposite membranes in contrast

to pure Aquivion®. However, Aq + CeO₂, and somewhat Aq + NH₂, are characterized by partial agglomeration of micrometric size clusters of CeO₂ NPs. In contrast, Aq + PF10 shows a more homogeneous distribution of CeO₂ NPs, probably because of the higher compatibility between the CeO₂ NPs decorated with fluorinated sidechains and Aquivion®'s structure. The cross section of the Aq + CeO₂ membrane, shown in Fig. S10, confirms the presence of micrometric-sized agglomerate of bare CeO₂ NPs. However, EDX spectra taken in regions where such a big agglomeration is absent still show the cerium signal around 4.8 keV (see inset of Fig. S10). We conclude that some nanoparticles agglomerate to give clusters, but a finer sub-micrometric size dispersion of Ce, in the form of CeO₂, is still present in the nanocomposite samples.

A comparison between XPS and SEM-EDX results indicates that the NPs are not located on the membrane surface; instead, they are embedded within the polymer strands at a depth of at least several tens of nanometers. This is deduced from the fact that the penetration depth of XPS is at most 10 nm, and no Ce was detected, while SEM-EDX maps highlighted the presence of Ce. This, apparent, discrepancy is readily explained considering that penetration depth of SEM-EDX is up to micrometers. This subsurface positioning is advantageous, as oxide particles in close proximity to the surface could hinder the formation of an effective triple phase boundary with fuel cell electrodes. Furthermore, this configuration prevents potential leaching of the filler at the electrode interface.

3.3. Functional characterization of the membranes

We measured the mechanical response to traction with stress-strain measurements in ambient conditions. The results are affected by a large statistical variation, and no clear trend appears as a function of the particle functionalization (see Fig. S11 and Table 4). Overall, the presence of the CeO₂ NPs increases the elastic modulus value, as expected [65,66].

Fig. 4 illustrates the WU and SR of the membranes as a function of temperature. The graph on the left reveals that the WU trend for all nanocomposite samples is approximately linear with temperature and mirrors that of the pristine Aquivion®. However, the nanocomposites exhibit lower absolute values across the entire temperature range, with Aq + PF10 showing the lowest slope. This overall behavior is expected, as the incorporation of inorganic fillers increases the total mass of the membrane, whereas the concentration of hydrophilic sulfonic groups remains constant. In contrast, the SR graph highlights a clear divergence between the nanocomposite PEMs and the pristine Aquivion®. As a matter of fact, Aquivion® displays a steep slope, indicating significant geometrical deformation as temperature rises. In contrast, the nanocomposite membranes show only a moderate increase in SR up to 80 °C. This mechanical stabilization is likely attributable to the inorganic

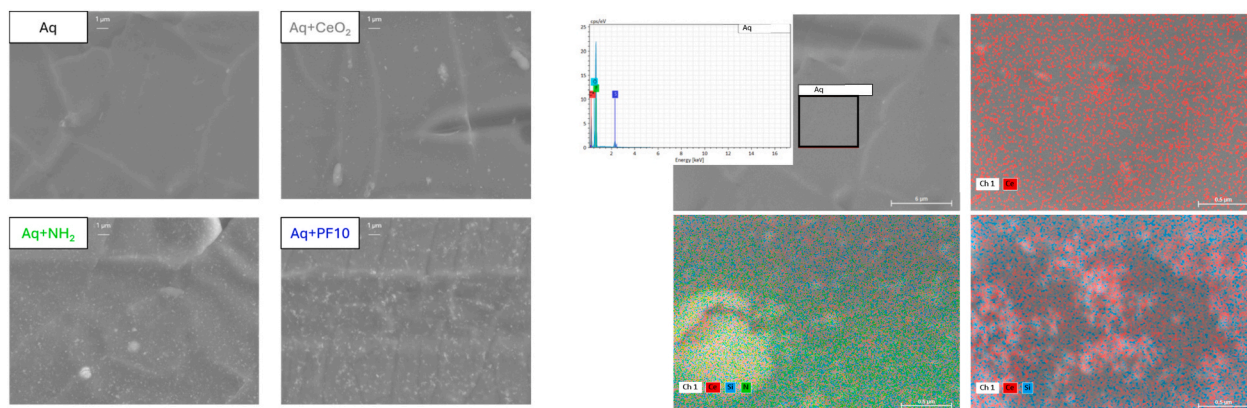


Fig. 3. Left: SEM images of the surface of four significant samples: pure Aq, Aq + CeO₂ with bare nanoparticles and two examples of decorated NP (Aq + NH₂ and Aq + PF10). Right: backscattered images of the same samples. The EDX analysis refers to the pure Aquivion® polymer.

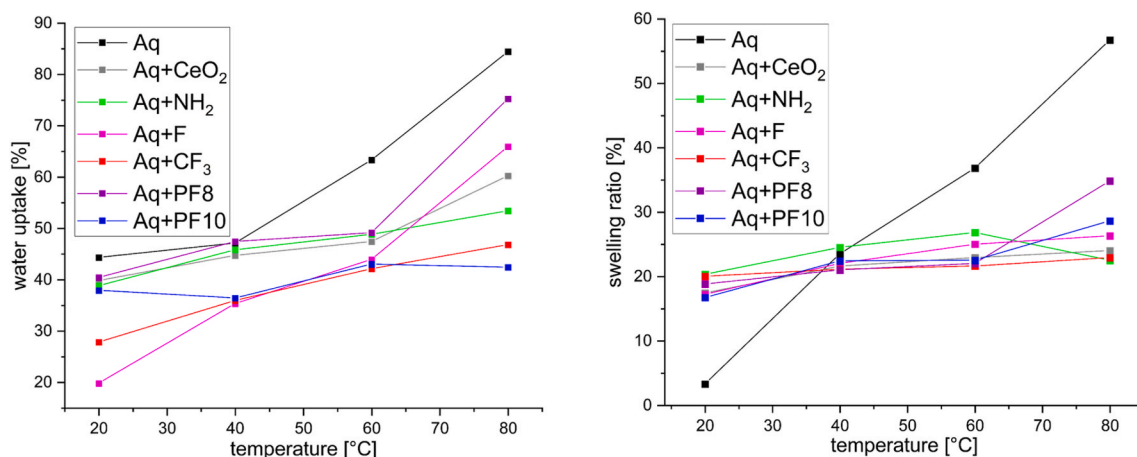


Fig. 4. Water absorption properties of the membranes. Left: water uptake. Right: swelling ratio.

nanoparticles acting as structural anchors that restrict polymer chain mobility. Unlike the flexible polymer matrix, these rigid inclusions resist deformation, thereby constraining the overall expansion. The observation that this effect is not further enhanced by the surface functionalization suggests that the grafting percentage is insufficient to significantly impact the bulk mechanical properties.

Fig. 5 shows the ionic conductivity of the membranes vs. temperature and relative humidity. The values reported in the left graph are the average between the heating up and cooling down segments of the ramp (see Supporting Information). The same is done for the curves on the right side, where the segments are drying up and re-hydrating at a constant temperature of 80 °C.

The conductivity of pure Aquivion® is consistent with literature reports regarding both temperature [67] and humidity dependence [48]. While the dependence on temperature is roughly linear within the explored range, the dependence on humidity is non-linear. Notably, the Aq + CeO₂ nanocomposite outperforms pure Aquivion® across all humidity levels at high temperatures, despite its relatively high loading of 5 wt%. This is significant as the literature [45,48,49] typically identifies an optimal CeO₂ loading between 1 and 3%, with higher concentrations usually decreasing conductivity due to dilution effects. Our membrane's performance may be attributed to the preparation process and annealing temperature, which likely enhanced the connectivity between hydrophilic clusters. Furthermore, pristine CeO₂, with its available hydroxyl groups, may contribute to proton conductivity at low humidity, a regime where water scarcity often compromises ionic channel interconnection. This hypothesis is further supported by the fact that Aq + F and Aq +

NH₂ are the least conductive samples, as their CeO₂ surfaces are more densely covered by functional groups. Furthermore Aq + NH₂ is expected to interact with the sulphonic end-groups of the polymer's side-chains hindering the conductivity mechanisms. The three samples featuring fluoroalkyl chains on CeO₂ show intermediate and similar behavior, particularly regarding relative humidity, both because of the lower surface coverage and of the weak interaction of the decoration with the Aquivion® backbone; rather than its sulphonic groups. Nevertheless, all samples exhibit conductivity values high enough to be considered promising for practical applications under 80 °C and 100% RH operating conditions.

Ex-situ chemical stability against oxidative radical attack was investigated via Fenton tests, with results presented in Fig. 6.

As expected, the incorporation of CeO₂ into the six nanocomposite membranes enhances their resistance to radical species compared to pure Aquivion®. Most membranes exhibited a ~50% reduction in fluoride emission, with the exceptions of Aq + F and Aq + CF₃, where fluoride emission remained closer to that of pristine Aquivion®. In the case of Aq + F, this behavior may be attributed to the grafting percentage of CeO₂+Si-F NPs, which is significantly higher than in other samples (Table 3). This high degree of functionalization reduces the number of "free" Ce (III) surface sites, thereby diminishing their efficacy as radical scavengers. While Aq + NH₂ presents a similar grafting profile, its performance is sustained by its higher filler loading, whereas Aq + F has the lowest (Table 4). Thus, in Aq + NH₂, high loading compensates for lower individual scavenging activity; conversely, in Aq + F, low loading and reduced site availability combine to limit protection.

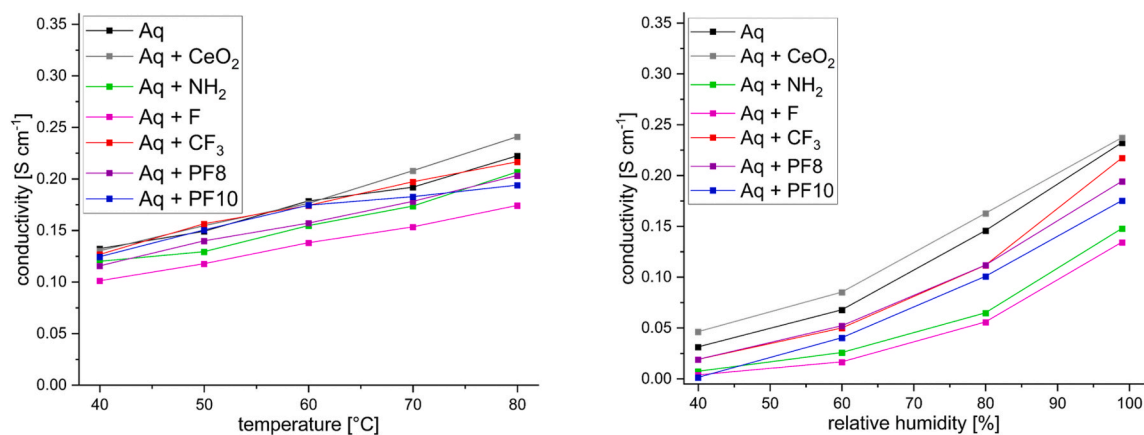


Fig. 5. Left: ionic conductivity of the membranes vs temperature at a constant 100% RH, averaged over heating and cooling down. Right: ionic conductivity at 80 °C vs relative humidity. The samples are stabilized 3 h at each temperature and or hydration level.

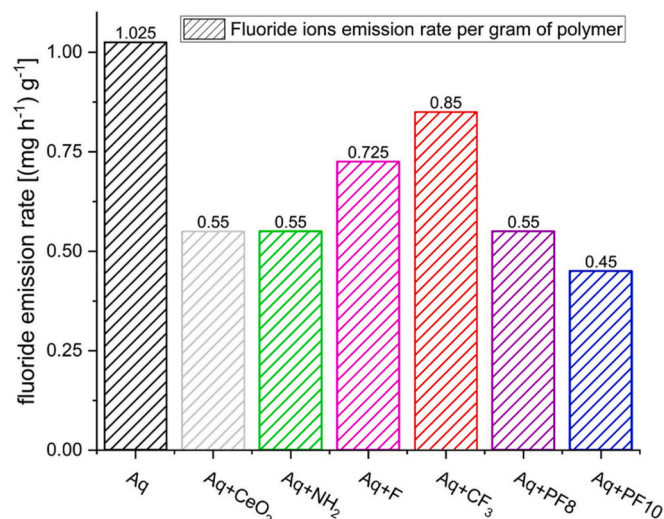


Fig. 6. Fenton test results reported as milligrams of F⁻ ions, normalized per gram of sample, emitted every hour.

While the behavior of Aq + CF₃ remains currently unclear, given its comparable decoration and loading to Aq + PF₈ and Aq + PF₁₀, the results for the latter two are highly promising. In fact, Aq + PF₈ and Aq + PF₁₀ showed reductions of 46% and 56%, respectively. This is particularly noteworthy as Aq + CeO₂ (bare NPs) possesses the highest concentration of Ce (III) sites and the second-highest loading and yet is not the best performing. Consequently, the chemical stability of Aq + PF₈ and Aq + PF₁₀ combined with their conductivity values, near to those of Aquivion®, reduced swelling, and more homogeneous filler dispersion, marks them as the most encouraging candidates for fuel cell application. We can also state that decorating the filler with fluoroalkyl moieties does not hinder radical scavenging, provided the functionalization remains within 10–20% of the hydroxyl sites.

3.4. Fuel cell performances and durability

MEAs were prepared with all the investigated membranes, as reported in the Experimental Section, and characterized with a segmented fuel cell. Fig. 7 shows the polarization curves together with the power

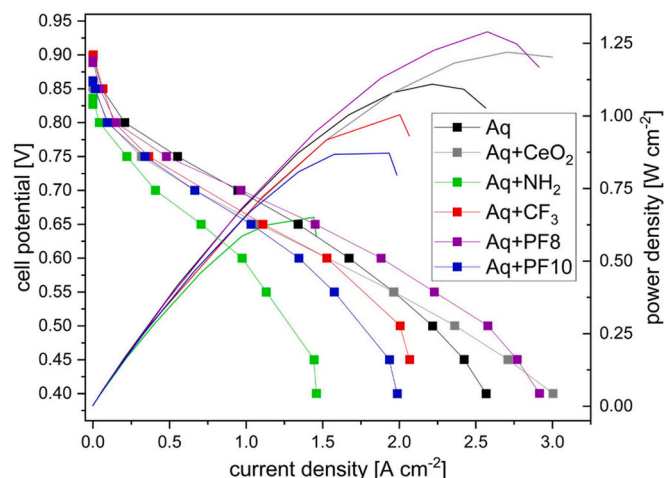


Fig. 7. Square symbols: polarization curves measured on MEAs with 0.3 mg cm⁻² Pt load on both electrodes, scanning from OCV to 0.4 V with 50 mV steps every 3 min. Straight lines: corresponding power densities. Working conditions: 80 °C, in 100% RH flowing H₂ at the anode side and air at the cathode side with a stoichiometry of 2:5.

densities.

Except for Aq + NH₂, the performance of all samples is promising. This sample's distance in performances to the others was expected as its conductivity was also lower. The reason could be found in the electron-donating characteristics of the decoration's end group that interacts with the sulphonic sidechains of Aquivion® through an acid-base reaction, in turn reducing the available protons and blocking a -SO₃ site. The best-performing MEAs achieved peak power densities exceeding 1 W cm⁻² using air at the cathode with moderate Pt loading. The polarization behavior followed the expected trend, with mass transport overpotentials becoming evident below 0.6 V. In detail, MEAs incorporating Aq + PF₁₀ and Aq + CF₃ exhibited lower performance than those based on pristine Aquivion®, whereas Aq + CeO₂ and Aq + PF₈ showed superior results. These findings correlate well with conductivity measurements, where Aq + CeO₂ maintained values like the pure polymer, followed closely by the membranes containing fluorinated NPs. This correlation is further supported by the polarization curves at 60% RH (Fig. S13), where the performance trends closely match the conductivity vs. RH profiles. Detailed fuel cell performance metrics are summarized in Table S2. Based on their overall balance of properties, including NPs homogeneous distribution, polarization behavior, conductivity, SR, and oxidative stability (Fenton test), Aq + PF₈ and Aq + PF₁₀ were identified as the most promising candidates, and were selected for comparison with the reference Aquivion® in an *in-situ* AST (Fig. 8).

In Table 5 the most promising results from this paper are reported and compared to recent and relevant literature employing PFSA polymer and Ce-based radical scavenger species. Notably the only samples outperforming these ones on all properties are those where the membrane is also mechanically reinforced; this is because this allows it to be thinner, and thus perform better, while reducing the gas crossover and the dimensional changes that are detrimental to the lifetime as they impact both chemical and mechanical degradation.

The OCV loss overtime during the AST of the two most promising decorated NPs nanocomposite samples are compared to the reference material in Fig. 8.

Fig. 8 shows the comparison between pure Aquivion®, Aq + PF₈ and Aq + PF₁₀. The difference in the behavior of the samples is evident: in the first 60 h the MEA bearing Aquivion® 720 membrane loses more than 10 mV in a linear fashion; after that, the drop is even steeper, probably due to the formation of pinholes causing the gas crossover to increase dramatically (see Table 6). On the other hand, the degradation

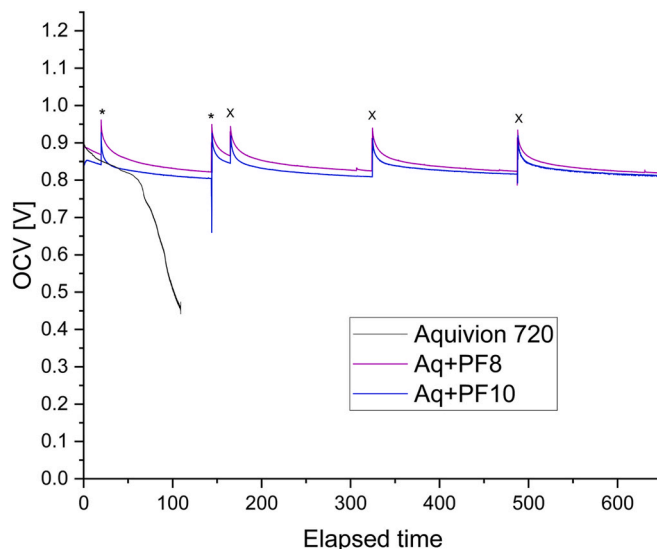


Fig. 8. AST of the two most promising samples Aq + PF₈ and Aq + PF₁₀ compared to pure Aquivion®. X indicates an interruption in the measurement to ascertain the H₂ current cross-over values; * indicates a power-shortage.

Table 5

Performances of the most promising samples and some relevant literature reported systems: power density at 0.6 V, peak power density and loss of OCV after AST.

Sample name	P @ 0.6V [W cm ⁻²]	P ^{MAX} [W cm ⁻²]	OCV loss [mV]	ref [n]
^a Aq	1.0	1.1 @ 0.45 V	450 @ 125 h	This work
^a Aq + PF8	1.1	1.3 @ 0.5 V	50 @ 650 h	This work
^b Aquivion®	1.2	1.48 @ 0.4 V	230 @ 100 h	[45]
^b Aq-f-CeO ₂ 0.5% wt	1.2	1.45 @ 0.45 V	150 @ 100 h	[45]
^c R79-02S	0.72	/	>300 @ 225 h	[40]
^c R79-02S + Ce @SiO ₂ -SO ₃ H	0.65	/	250 @ 1400 h	[40]
^d AQ e-PTFE#	0.45	0.61 @ 0.4 V	280 @ 48 h	[43]
^d AQ e-PTFE +1%Pt/CeO ₂ #, *	0.7	0.95 @ 0.5 V	280 @ 78 h	[43]
^e NR211 Pt/C	0.97	1.08 @ 0.5 V	200 @ 176 h	[30]
^e NR211 Pt/C CeHP (3.8%) *	0.69	0.9 @ 0.45 V	50 @ 500 h	[30]
^f N211#	1.3	1.5 @ 0.5 V	100 @ 1200 h	[26]
^f Ce ₂ MnNH ₂ BDC@PFSA#	1.5	1.6 @ 0.5 V	40 @ 1200 h	[26]
^g Gore-select#	1.3	1.84 @ 0.5 V	180 @ 40 h	[46]
^g PFSA/d-Uio-66# *	1.7	1.91 @ 0.55 V	100 @ 100 h	[46]
^h N211	0.7	0.78 @ 0.5 V	300 @ 72 h	[35]
^h Nafion®-Ce@15C5-ePTFE-2#	0.8	0.85 @ 0.55 V	200 @ 250 h	[35]

#indicates the use of a reinforced membrane.

*indicates that the Ce-based radical scavenger is in the catalyst layer and not in the membrane itself.

^a T = 80 °C, 100% RH, 0.3 mg cm⁻² Pt/C, H₂/air 2/5, 2.3 bar_{gauge}. AST: T = 90 °C, 30%RH, 0.5 mg cm⁻² Pt/C, H₂/air 2/5, 0.5 bar_{gauge}.

^b T = 65 °C, 100% RH, 0.5 mg cm⁻² Pt/C, H₂/O₂ 1.2/3. AST: T = 85 °C, 30% RH, 0.5 mg cm⁻² Pt/C, H₂/air 70/100.

^c T = 75 °C, 65% RH, 0.5 mg cm⁻² Pt/C, H₂/air, 1.0 bar_{abs}. AST: T = 90 °C, 30% RH, 0.5 mg cm⁻² Pt/C, H₂/O₂, 1.0 bar_{abs}.

^d T = 80 °C, 50% RH, 0.2 mg cm⁻² Pt/C, H₂/air 1.5/2, 2.0 bar_{abs}. AST: T = 90 °C, 30%RH, 0.2 mg cm⁻², H₂/air, 1.5 bar_{abs}.

^e T = 80 °C, 100% RH, 0.4 mg cm⁻² Pt/C, H₂/air 0.7/1.5, 101 kPa. AST: T = 90 °C, 30%RH, 0.5 mg cm⁻² Pt/C, H₂/air 10/10, 101 kPa.

^f T = 90 °C, 100% RH, 0.1/0.3 mg cm⁻² Pt/C, H₂/air 1.3/2, 0.1 MPa. AST: T = 90 °C, 30%RH, 0.1/0.3 mg cm⁻², H₂/air 1.3/2, 0.1 MPa.

^g T = 70 °C, 100% RH, 0.1/0.3 mg cm⁻² Pt/C, H₂/air, 0.7 bar. AST: T = 90 °C, 30%RH, 0.1/0.3 mg cm⁻², H₂/air 1.3/2, 1.1 bar.

^h T = 65 °C, 100% RH, 0.3 mg cm⁻² Pt/C, H₂/air 1.5/2. AST: T = 90 °C, 30% RH, 0.3 mg cm⁻², H₂/air, 150 kPa.

Table 6

H₂ crossover current measured at different times during the OCV-hold AST. * Indicates that the measurement was performed after the samples' failure at 110 h.

I _{cross} H ₂ [mA cm ⁻²]	t = 0 h	t = 168 h	t = 336 h	t = 504 h
Aq	1.4 ± 0.2	275*	/	/
Aq + PF8	1.0 ± 0.2	1.4 ± 0.4	1.4 ± 0.4	1.3 ± 0.4
Aq + PF10	3.7 ± 0.7	4.0 ± 0.9	4.1 ± 0.9	4.0 ± 0.9

of the MEA containing Aq + PF8 and Aq + PF10 is negligible after more than 650h. The latter starts at OCV $\cong$ 0.85V and loses roughly 50 mV over the course of 650 h, dropping to around 0.8 V. Aq + PF8 has an initial OCV $\cong$ 0.9 V but ends up around 0.8 V too after the same time.

The average OCV loss is, respectively, 0.15 mV h⁻¹ and 0.08 mV h⁻¹ for Aq + PF8 and Aq + PF10 over more than 650 h which is between 10 and 20 times lower than literature reports for similar timescales [44], and still better than some reports after less than 100h [45]. This result, although preliminary, is very encouraging.

Table 6 shows the crossover currents measured on the same samples of Fig. 8. At the beginning of the AST, all the samples showed values well below the U.S. Department of Energy failure condition of 15 mA cm⁻². Whereas the Aquivion® membrane clearly failed already after 110 h (see Caption), the other ones showed nearly constant values for more than 500 h.

While it is not simple to obtain *post-mortem* evidence of possible NPs (or dissolved Ce ions) migration due to the problems related to MEA detachment, we performed an in-plane cerium ions migration measurement on Aq + PF10 as a preliminary investigation of the risk of accumulation of cerium during operation in a fuel cell. A sample was subjected to a hydrogen pumping test, after which we studied the cerium concentration along the membrane with XRF. The results are reported in Fig. 9.

The figure clearly shows that there is no accumulation of cerium in the direction where in-plane migration is supposed to occur. This hints at a far superior stability, in this regard, to cerium ion doped PEMs where migration is known to occur meaningfully in similar tests [57]. The apparent patterning seen in the image is caused by the transfer of the support used while pressing the catalyst layers on the sample for the H₂ pumping test.

4. Conclusions

In this study, we demonstrated that the functionalization of CeO₂ NPs with fluoroalkylic moieties is an effective strategy for enhancing the durability of Aquivion®-based PEMFCs without compromising their electrochemical performance. The rational design of the nanoparticle surface allowed for a balance between filler-polymer compatibility and radical scavenging efficiency. Specifically, fluoroalkyl silanes with longer side chains, such as Aq + PF8 and Aq + PF10 sample, provided an optimal configuration by maintaining high proton conductivity, comparable to pristine Aquivion®, while achieving a significant reduction (up to 56%) in fluoride emission rates during *ex-situ* Fenton tests. Surface decoration not only improved the dispersion of NPs within the

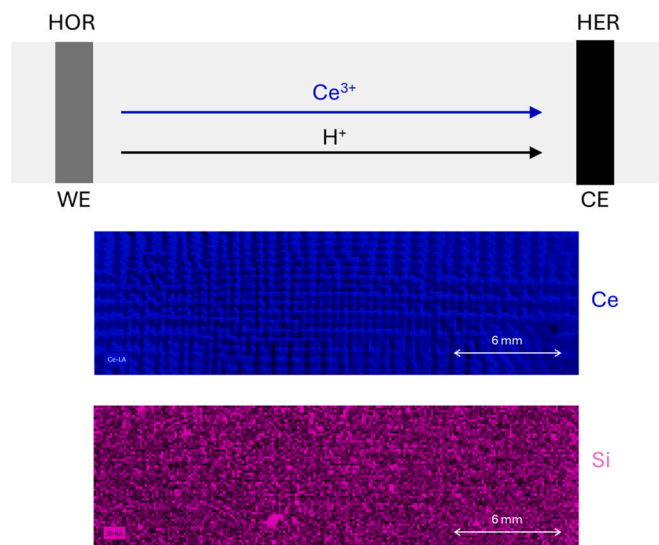


Fig. 9. XRF maps of cerium and silicon, after the hydrogen pumping for 15 h at 80 °C, 100% RH (see Experimental Section). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

polymer matrix but also helped integrate them into the hydrophobic domains. This minimized the disruption of ionic channels, as evidenced by conductivity values exceeding 150 mS cm^{-1} at 80°C and 100% RH. Furthermore, the best-performing MEAs reached peak power densities over 1 W cm^{-2} , demonstrating that these nanocomposites are competitive with state-of-the-art materials. The AST conducted for over 600 h revealed negligible degradation of the most promising samples indicating that these membranes remained largely intact under the tested conditions. To overcome the difficulties associated with making reliable *post-mortem* measurements, we investigated cerium migration by means of XRF mapping following hydrogen pumping. This highlighted negligible scavenger dissolution, at least in the limits of the chosen experimental protocol. Future studies will involve even more aggressive and/or prolonged AST protocols to reach a degradation threshold that allows in-depth *post-mortem* investigations.

CRedit authorship contribution statement

Diego Stucchi: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Alessandro R. Ferrari:** Methodology, Conceptualization. **Tommaso Caielli:** Methodology, Conceptualization. **Antonio G. Di Tolla:** Investigation. **Rodrigo Schneider:** Methodology. **Marc Dupont:** Writing – review & editing, Resources. **Daniele Mora:** Methodology, Investigation. **Elena Colombo:** Methodology, Investigation. **Gioele Pagot:** Writing – review & editing, Methodology, Investigation. **Vito Di Noto:** Resources. **Andrea Baricci:** Resources. **Sara Cavaliere:** Writing – review & editing, Resources. **Piercarlo Mustarrelli:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition.

Data availability statement

Data will be available on request.

Declaration of competing interest

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

Acknowledgements

This work received funding from the Italian government (Ministero dell'Ambiente e della Sicurezza Energetica), under the project PERMANENT - Bando MITE PNRR Missione 2 Investimento 3.5 A - RSH2A 000012.

The authors also acknowledge Syensqo (D. Facchi and M. Messaggi) for providing the commercial Aquivion® dispersion and their support in the fabrication of the membranes, the preparation of the CCMs, and the durability measurement, within the PERMANENT project.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2026.158193>.

References

- [1] Hydrogen and fuel cell technologies office, Ed., 'DOE Technical Targets for Fuel Cell Systems and Stacks for Transportation Applications'.
- [2] European Commission: Directorate-General for Energy. Design, development and implementation of joint purchasing options under EU energy platform – final report. et al. Publications Office of the European Union; 2024. <https://doi.org/10.2833/4362329>.
- [3] Du L, Prabhakaran V, Xie X, Park S, Wang Y, Shao Y. Low-PGM and PGM-free catalysts for proton exchange membrane fuel cells: stability challenges and

material solutions. *Adv Mater Feb.* 2021;33(6):1908232. <https://doi.org/10.1002/adma.201908232>.

- [4] Li Y-S, Menga D, Gasteiger HA, Suthar B. Design of PGM-free cathode catalyst layers for PEMFC applications: the impact of electronic conductivity. *J Electrochem Soc Sep.* 2023;170(9):094503. <https://doi.org/10.1149/1945-7111/acfd3>.
- [5] Stassi A, et al. Performance comparison of long and short-side chain perfluorosulfonic membranes for high temperature polymer electrolyte membrane fuel cell operation. *J Power Sources Nov.* 2011;196(21):8925–30. <https://doi.org/10.1016/j.jpowsour.2010.12.084>.
- [6] Talukdar K, Gazdzicki P, Friedrich KA. Comparative investigation into the performance and durability of long and short side chain ionomers in polymer electrolyte membrane fuel cells. *J Power Sources Nov.* 2019;439:227078. <https://doi.org/10.1016/j.jpowsour.2019.227078>.
- [7] Young AP, Stumper J, Gyenge E. Characterizing the structural degradation in a PEMFC cathode catalyst layer: carbon corrosion. *J Electrochem Soc Jun.* 2009;156(8):B913. <https://doi.org/10.1149/1.3139963>.
- [8] He W, Tang F, Li X, Zhang C, Ming P. Quantification and evolution on degradation mechanisms of proton exchange membrane fuel cell catalyst layer under dynamic testing conditions. *Int J Hydrogen Energy Jun.* 2023;48(47):18032–40. <https://doi.org/10.1016/j.ijhydene.2023.01.109>.
- [9] LaConti AB, Hamdan M, McDonald RC. Mechanisms of membrane degradation. In: *Handbook of fuel cells*; 2010. <https://doi.org/10.1002/9780470974001.f303055>.
- [10] Healy J, et al. Aspects of the chemical degradation of PFSA ionomers used in PEM fuel cells. *Fuel Cells Apr.* 2005;5(2):302–8. <https://doi.org/10.1002/fuce.200400050>.
- [11] Huang X, et al. Mechanical endurance of polymer electrolyte membrane and PEM fuel cell durability. *J Polym Sci B Polym Phys Aug.* 2006;44(16):2346–57. <https://doi.org/10.1002/polb.20863>.
- [12] Subianto S, et al. Physical and chemical modification routes leading to improved mechanical properties of perfluorosulfonic acid membranes for PEM fuel cells. *J Power Sources Jul.* 2013;233:216–30. <https://doi.org/10.1016/j.jpowsour.2012.12.121>.
- [13] Alberti G, Narducci R, Di Vona ML, Giancola S. Annealing of nafion 1100 in the presence of an annealing agent: a powerful method for increasing ionomer working temperature in PEMFCs. *Fuel Cells Feb.* 2013;13(1):42–7. <https://doi.org/10.1002/fuce.201200126>.
- [14] Giancola S, et al. Study of annealed Aquivion® ionomers with the INCA method. *Membranes* 2019;9(10). <https://doi.org/10.3390/membranes9100134>.
- [15] Sood R, Cavaliere S, Jones DJ, Rozière J. Electrospun nanofibre composite polymer electrolyte fuel cell and electrolysis membranes. *Nano Energy Aug.* 2016;26:729–45. <https://doi.org/10.1016/j.nanoen.2016.06.027>.
- [16] Nicotera I, Coppola L, Simari C. Enhancing sulfonated polyethersulfone performance by incorporating TiO₂-decorated MWCNTs: a viable solution for high-temperature polymer electrolyte fuel cell applications. *Int J Hydrogen Energy Nov.* 2024;49:56–65. <https://doi.org/10.1016/j.ijhydene.2024.09.282>.
- [17] Coms FD. The chemistry of fuel cell membrane chemical degradation. *ECS Trans Oct.* 2008;16(2):235–55. <https://doi.org/10.1149/1.2981859>.
- [18] Gubler L, Dockheer SM, Koppenol WH. Radical (HO•, H• and HOO•) formation and ionomer degradation in polymer electrolyte fuel cells. *J Electrochem Soc Apr.* 2011;158(7):B755. <https://doi.org/10.1149/1.3581040>.
- [19] Endoh E. Development of highly durable PFSA membrane and MEA for PEMFC under high temperature and low humidity conditions. *ECS Trans Oct.* 2008;16(2):1229. <https://doi.org/10.1149/1.2981964>.
- [20] Trogadas P, Parrondo J, Ramani V. Degradation mitigation in polymer electrolyte membranes using free radical scavengers. *ECS Trans Oct.* 2008;16(2):1725. <https://doi.org/10.1149/1.2982014>.
- [21] Zhu Y, Mai J, Li H, Tang J, Yuan WZ, Zhang Y. Enhanced stability of PFSA membranes for fuel cells: combined effect between supercritical carbon dioxide treatment and radical scavenger incorporation. *Polym Degrad Stab Sep.* 2014;107:106–12. <https://doi.org/10.1016/j.polydegradstab.2014.05.006>.
- [22] Coms FD, Liu H, Owejan JE. Mitigation of perfluorosulfonic acid membrane chemical degradation using cerium and manganese ions. *ECS Trans Oct.* 2008;16(2):1735. <https://doi.org/10.1149/1.2982015>.
- [23] Danileczuk M, Schlick S, Coms FD. Cerium(III) as a stabilizer of perfluorinated membranes used in fuel cells: in situ detection of early events in the ESR resonator. *Macromolecules* 2009;42(22):8943–9. <https://doi.org/10.1021/ma9017108>.
- [24] Zhao D, Yi BL, Zhang HM, Yu HM. MnO₂/SiO₂-SO₃H nanocomposite as hydrogen peroxide scavenger for durability improvement in proton exchange membranes. *J Membr Sci Jan.* 2010;346(1):143–51. <https://doi.org/10.1016/j.memsci.2009.09.031>.
- [25] Paul S, Choi S-J, Kim HJ. Co-tri MOF-impregnated Aquivion® composites as proton exchange membranes for fuel cell applications. *Ionics Apr.* 2021;27(4):1653–66. <https://doi.org/10.1007/s11581-021-03923-3>.
- [26] Huang H, Zhong Z, Li J, Li H. A manganese-doped cerium-based metal-organic framework as a radical scavenger for proton exchange membrane fuel cells with superior stability. *ACS Appl Energy Mater Dec.* 2024;7(23):10804–14. <https://doi.org/10.1021/acsaeam.4c01502>.
- [27] Trogadas P, Parrondo J, Ramani V. Degradation mitigation in polymer electrolyte membranes using cerium oxide as a regenerative free-radical scavenger. *Electrochem Solid State Lett* 2008;11(7):B113. <https://doi.org/10.1149/1.2916443>.
- [28] Gubler L, Koppenol WH. Kinetic simulation of the chemical stabilization mechanism in fuel cell membranes using cerium and manganese redox couples. *J Electrochem Soc* 2012;159(2):B211–8. <https://doi.org/10.1149/2.075202jes>.

- [29] Rui Z, Liu J. Understanding of free radical scavengers used in highly durable proton exchange membranes. *Prog Nat Sci Mater Int* Dec. 2020;30(6):732–42. <https://doi.org/10.1016/j.pnsc.2020.08.013>.
- [30] Lee B-N, Lim KH, Hong JW, Lee SY, Han J, Kim H-J. Enhancing the chemical durability of perfluorosulfonic acid membranes using cerium-based radical scavengers coordinated with hydrogen phosphate groups. *J Power Sources* Dec. 2026;695:241352. <https://doi.org/10.1016/j.jpowsour.2026.241352>.
- [31] Baker AM, et al. Cerium migration during PEM fuel cell assembly and operation. *ECS Trans* Sep. 2015;69(17):1009–15. <https://doi.org/10.1149/06917.1009ecst>.
- [32] Zatoň M, Prélôt B, Donzel N, Rozière J, Jones DJ. Migration of Ce and Mn ions in PEMFC and its impact on PFSA membrane degradation. *J Electrochem Soc* 2018; 165(6):F3281–9. <https://doi.org/10.1149/2.0311806jes>.
- [33] Yuk S, et al. Detrimental effect of Ce⁴⁺ ion on the Pt/C catalyst in polymer electrolyte membrane fuel cells. *J Power Sources* Feb. 2020;448:227447. <https://doi.org/10.1016/j.jpowsour.2019.227447>.
- [34] Agarwal T, et al. Mitigating cerium migration for perfluorosulfonic acid membranes using organic ligands. *J Power Sources* Jan. 2023;554:232320. <https://doi.org/10.1016/j.jpowsour.2022.232320>.
- [35] Lee Y, Yuk M, Kim T-H, Kim S-K. Spray-coated cerium-loaded crown ether layers on expanded PTFE for reinforced composite fuel cell membranes with improved durability. *Appl Surf Sci* Nov. 2026;745:167443. <https://doi.org/10.1016/j.apsusc.2026.167443>.
- [36] Wang G, Parrondo J, Ramani V. Stabilization of perfluorinated membranes using nanoparticle additives. In: *The chemistry of membranes used in fuel cells*; 2018. p. 139–69. <https://doi.org/10.1002/9781119196082.ch6>.
- [37] Yoon KR, et al. Mussel-inspired polydopamine-treated reinforced composite membranes with self-supported CeO_x radical scavengers for highly stable PEM fuel cells. *Adv Funct Mater* Jan. 2019;29(3):1806929. <https://doi.org/10.1002/adfm.201806929>.
- [38] Le ML, Irshad M, Duong TT, Park MH, Lee CH, Kim J. Nano-redispersible metal-oxide-ionomer composite nanopowders prepared using perfluorinated sulfonic acid ionomers in anion-exchange membrane and their radical scavenging performance. *Macromol Res* Apr. 2024;32(4):299–311. <https://doi.org/10.1007/s13233-023-00230-w>.
- [39] Siracusano S, Giacobello F, Tonella S, Oldani C, Aricò AS. Ce-radical scavenger-based perfluorosulfonic acid Aquivion® membrane for pressurised PEM electrolyzers. *Polymers* Jan. 2023;15(19):3906. <https://doi.org/10.3390/polym15193906>.
- [40] D'Urso C, Oldani C, Baglio V, Merlo L, Aricò AS. Towards fuel cell membranes with improved lifetime: Aquivion® perfluorosulfonic acid membranes containing immobilized radical scavengers. *J Power Sources* Dec. 2014;272:753–8. <https://doi.org/10.1016/j.jpowsour.2014.09.045>.
- [41] Akrot A, et al. Immobilisation and release of radical scavengers on nanoclays for chemical reinforcement of proton exchange membranes. *Membranes* 2020;10(9). <https://doi.org/10.3390/membranes10090208>.
- [42] Xing Y, Liu L, Fu Z, Li Y, Li H. High-performance and durable membrane electrode assemblies based on CeO₂ and ePTFE double-reinforcement strategy for proton exchange membrane fuel cells operating at elevated temperatures. *J Power Sources* Dec. 2023;587:233727. <https://doi.org/10.1016/j.jpowsour.2023.233727>.
- [43] Gatto I, et al. Improved durability of MEAs based on Aquivion® and radical scavenger for polymer electrolyte fuel cells. *Electrochim Acta* May 2026;559: 148590. <https://doi.org/10.1016/j.electacta.2026.148590>.
- [44] D'Amato R, et al. Polydopamine coated CeO₂ as radical scavenger filler for aquivion® membranes with high proton conductivity. *Materials* 2021;14(18). <https://doi.org/10.3390/ma14185280>.
- [45] Dass BM, Neeshma M, Unni SM, Dhavale VM, Prabhakaran D, Bhat SD. Functionalized Ceria nanoparticles reinforced with short side chain-based composite membrane for low-humidity hydrogen-powered fuel cells. *ACS Appl Polym Mater* Oct. 2024;6(19):11691–705. <https://doi.org/10.1021/acsp.4c02106>.
- [46] Tu Z, et al. Missing-linker defects of Ce-Uio-66 for enhanced radical scavenging efficiency and proton conductivity in proton exchange membrane fuel cells. *Chem Eng J* Feb. 2025;505:159357. <https://doi.org/10.1016/j.cej.2025.159357>.
- [47] Sypabekova M, Hagemann A, Rho D, Kim S. Review: 3-aminopropyltriethoxysilane (APTES) deposition methods on oxide surfaces in solution and vapor phases for biosensing applications. *Biosensors* 2023;13(1):36. <https://doi.org/10.3390/bios13010036>.
- [48] Donnadio A, et al. On the evolution of proton conductivity of aquivion® membranes loaded with CeO₂ based nanofillers: effect of temperature and relative humidity. *J Membr Sci* Mar. 2019;574:17–23. <https://doi.org/10.1016/j.memsci.2018.12.045>.
- [49] Safronova E Yu, Yaroslavtsev AB. Aquivion hybrid membranes modified with hydrated oxides MO₂ (M = Si, Ti, Ce): transport properties and chemical stability. *Membr Membr Technol* Oct. 2024;6(5):325–31. <https://doi.org/10.1134/S251775162460081X>.
- [50] Di Noto V, Boaretto N, Negro E, Pace G. New inorganic–organic proton conducting membranes based on Nafion and hydrophobic fluoroalkylated silica nanoparticles. *J Power Sources* Dec. 2010;195(23):7734–42. <https://doi.org/10.1016/j.jpowsour.2009.10.028>.
- [51] Briggs D, Seah MP. *Practical surface analysis: auger and X-ray photoelectron spectroscopy*. second ed. New York: John Wiley & Sons; 1990.
- [52] Shirley DA. High-resolution X-Ray photoemission spectrum of the valence bands of gold. *Phys Rev B* 1972;5:4709–14.
- [53] Colombo E, Casadei D, Baricci A, Casalegno A. An open-source zero-gradient cell hardware to improve and accelerate durability testing of PEM fuel cells. *HardwareX* Dec. 2023;16:e00495. <https://doi.org/10.1016/j.ohx.2023.e00495>.
- [54] Casadei D, et al. Experimental investigation on the effect of channel geometry on performance heterogeneity in hydrogen PEM fuel cell. *Int J Hydrogen Energy* Dec. 2024;95:1299–315. <https://doi.org/10.1016/j.ijhydene.2024.08.515>.
- [55] Mora Daniele, Colombo Elena, Casalegno Andrea, Baricci Andrea. Evaluation of PEM Fuel Cell Degradation Through Accelerated Stress Tests to Investigate Heterogeneity of Ageing. *Journal of The Electrochemical Society* 2025;172(4): 044509. <https://doi.org/10.1149/1945-7111/adc62b>. <https://iopscience.iop.org/article/10.1149/1945-7111/adc62b>. [Accessed 16 April 2025].
- [56] Colombo Elena, Baricci Andrea, Mora Daniele, Guetaz Laure, Casalegno Andrea. An innovative accelerated stress test representative of automotive PEMFC degradation mechanisms validated on 1000 hours real-world operation. *Journal of Power Sources* 2023;580:233376. <https://doi.org/10.1016/j.jpowsour.2023.233376>. <https://linkinghub.elsevier.com/retrieve/pii/S0378775323007528>.
- [57] Verducci F, et al. Cerium in-plane transport in PEM fuel cells during real-world automotive operations: experimental and dynamic modelling analysis. *J Power Sources* Dec. 2025;660:238538. <https://doi.org/10.1016/j.jpowsour.2025.238538>.
- [58] Colombo E, et al. In-plane redistribution of radical scavenger during PEMFC real-world automotive operation and impact on catalyst-layer local oxygen transport resistance. *J Power Sources* Feb. 2025;629:235962. <https://doi.org/10.1016/j.jpowsour.2024.235962>.
- [59] Baker AM, et al. Cerium ion mobility and diffusivity rates in perfluorosulfonic acid membranes measured via hydrogen pump operation. *J Electrochem Soc* 2017;164 (12):F1272–8. <https://doi.org/10.1149/2.122171jes>.
- [60] Baker AM, Komini Babu S, Chintam K, Kusoglu A, Mukundan R, Borup RL. 'Ce Cation Migration and Diffusivity in Perfluorosulfonic Acid Fuel Cell Membranes'. *Sep. 2019*. <https://doi.org/10.1149/MA2019-02/34/1502>. Meet. Abstr., vol. MA2019-02, no. 34, pp. 1502–1502.
- [61] Verducci F, et al. Cerium in-plane transport in PEM fuel cells during real-world automotive operations: experimental and dynamic modelling analysis. *J Power Sources* Dec. 2025;660:238538. <https://doi.org/10.1016/j.jpowsour.2025.238538>.
- [62] Mostoni Silvia, D'Arienzo Massimiliano, Di Credico Barbara, Armelao Lidia, Rancan Marzio, Dirè Sandra, Callone Emanuela, Donetti Raffaella, Susanna Antonio, Scotti Roberto. Design of a Zn Single-Site Curing Activator for a More Sustainable Sulfur Cross-Link Formation in Rubber. *Industrial & Engineering Chemistry Research* 2021;60(28):10180–92. <https://doi.org/10.1021/acs.iecr.1c01580>. <https://pubs.acs.org/doi/10.1021/acs.iecr.1c01580>. [Accessed 7 July 2021].
- [63] Mezzomo Lorenzo, Bonato Stefano, Mostoni Silvia, Credico Barbara Di, Scotti Roberto, D'Arienzo Massimiliano, Mustarelli Piercarlo, Ruffo Riccardo. Composite solid-state electrolyte based on hybrid poly(ethylene glycol)-silica fillers enabling long-life lithium metal batteries. *Electrochimica Acta* 2022;411:140060. <https://doi.org/10.1016/j.electacta.2022.140060>. 140060, <https://linkinghub.elsevier.com/retrieve/pii/S0013468622002328>.
- [64] Kusoglu A, et al. Transport and morphology of a proton exchange membrane based on a doubly functionalized perfluorosulfonic imide side chain perfluorinated polymer. *Chem Mater* Jan. 2020;32(1):38–59. <https://doi.org/10.1021/acs.chemmater.8b05012>.
- [65] Hiemenz PC, Lodge TP. *Polymer chemistry*. second ed. Boca Raton: Taylor & Francis; 2007 [etc.].
- [66] Wang Z, et al. Synthesis of Nafion/CeO₂ hybrid for chemically durable proton exchange membrane of fuel cell. *J Membr Sci* 2012;421–422:201–10. <https://doi.org/10.1016/j.memsci.2012.07.014>.
- [67] Li Ting, Shen Jiabin, Chen Guangying, Guo Shaoyun, Xie Guangyou. Performance Comparison of Proton Exchange Membrane Fuel Cells with Nafion and Aquivion Perfluorosulfonic Acids with Different Equivalent Weights as the Electrode Binders. *ACS Omega* 2020;5(28):17628–36. <https://doi.org/10.1021/acsomega.0c02110>. <https://pubs.acs.org/acsodf/article/5/28/17628/583882/Performance-Comparison-of-Proton-Exchange-Membrane>. [Accessed 7 July 2020].