

Nanointerface-regulated cerium confinement via crown ether coordination in proton exchange membranes

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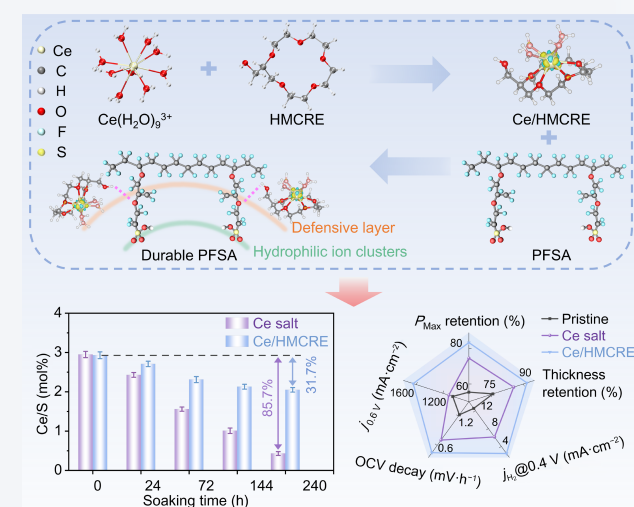
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ABSTRACT: Cerium (Ce)-based free radical scavengers, including soluble Ce^{3+} species, have been widely investigated to enhance the chemical durability of proton exchange membranes (PEMs) owing to their rapid and regenerative redox cycling. However, the high mobility of soluble Ce^{3+} ions in hydrated membranes leads to severe leaching, disruption of ion-cluster nanostructures, and degradation of PEM fuel cell (PEMFC) performance. Regulating the behavior of cerium species within the nanophase-separated environment of perfluorosulfonic acid (PFSA) membranes remains a critical challenge. Herein, we report a nanointerface-regulated cerium confinement strategy enabled by crown ether coordination. A model organometallic complex (Ce/HMCRE) is constructed using 2-(hydroxymethyl)-15-crown-5-ether (HMCRE), in which host-guest coordination and secondary hydrogen bonding interactions cooperatively modulate cerium distribution at polymer nanointerfaces. This coordination-mediated nanoconfinement effectively suppresses direct Ce^{3+} -sulfonate interactions while preserving the intrinsic ion-cluster morphology of PFSA membranes. As a result, the Ce/HMCRE complex exhibits significantly enhanced cerium retention (3.76 fold higher than free Ce^{3+}) together with sustained radical scavenging activity. The corresponding membrane electrode assembly delivers a low open circuit voltage decay rate of $0.45 \text{ mV} \cdot \text{h}^{-1}$ and retains 83.4% of its maximum power density after 150 h of accelerated degradation testing. This work highlights the importance of nanointerface engineering and confined microenvironments in regulating redox-active species within ionomer membranes, providing new insights into the design of durable electrochemical energy materials.

KEYWORDS: proton exchange membrane, nanointerface, cerium confinement, ion-cluster structure, crown ether coordination

1 Introduction

As a mature electrochemical energy conversion technology, proton exchange membrane fuel cells (PEMFCs) feature high energy



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conversion efficiency, near-zero emissions, high power density, and quiet operation, enabling their wide deployment in transportation, portable power sources, and stationary energy systems [1–7]. Despite substantial progress, the long-term durability of PEMs remains a critical bottleneck for PEMFC commercialization [8–10]. Within the membrane electrode assembly (MEA), the PEM simultaneously serves as a proton conductor and a physical barrier separating reactant gases, making its structural and chemical integrity essential for sustained operation [11, 12]. Perfluorosulfonic acid (PFSA) membranes are widely used owing to their excellent

proton conductivity and mechanical robustness [13, 14]. However, PFSA membranes possess a characteristic nanophase-separated structure composed of hydrophilic ion-cluster domains and hydrophobic polymer backbones, which is highly susceptible to chemical degradation induced by reactive oxygen species (ROS), such as hydroxyl ($\cdot\text{OH}$) and hydroperoxyl ($\cdot\text{OOH}$) radicals, generated from gas crossover and parasitic oxygen reduction reactions [15, 16]. Consequently, suppressing radical-induced chemical degradation and preserving the integrity of ion-cluster nanostructures under oxidative conditions is essential for achieving durable PEMs [17, 18].

Among various mitigation strategies, the incorporation of free radical scavengers (FRSs) has been extensively investigated to enhance the chemical stability of PEMs [19–22]. Cerium (Ce)-based species are particularly attractive due to the fast and regenerative redox cycling between Ce^{3+} and Ce^{4+} , which enables continuous scavenging of ROS [22]. Early work by Coms et al. demonstrated that introducing Ce^{3+} ions into MEAs via ion exchange significantly improved oxidative stability [23]. In acidic environments, Ce^{3+} reacts with $\cdot\text{OH}$ and $\cdot\text{OOH}$ radicals to form Ce^{4+} , which can subsequently be reduced back to Ce^{3+} by hydrogen peroxide, thereby sustaining the scavenging cycle [24]. Despite these advantages, the behavior of cerium species within the nanoconfined environment of PFSA membranes remains insufficiently understood.

A major limitation arises from the strong electrostatic interaction between multivalent Ce^{3+} ions and sulfonate groups ($-\text{SO}_3^-$), which can suppress proton mobility and deteriorate membrane conductivity as the cerium content increases [25, 26]. Moreover, when introduced through physical mixing or ion exchange, Ce^{3+} ions are only weakly confined within the membrane and tend to migrate toward the electrodes under concentration gradients and electric fields. Such migration not only poisons catalyst layers but also perturbs the ion-cluster nanodomains and disrupts interfacial transport pathways, ultimately leading to irreversible loss of radical scavengers and compromised durability [27]. These intrinsic trade-offs highlight the necessity of regulating cerium species within the nanostructured ionomer environment while preserving the native nanophase-separated architecture of PFSA membranes.

To address this issue, various cerium immobilization strategies have been proposed, including covalent grafting of chelating groups onto polymer backbones, surface-confined adhesive coatings, and the incorporation of strongly coordinating organic ligands [28–32]. Coordination compounds based on dipicolinate [33], cyclic ligands [34, 35], quercetin [36], and phosphonic acids [37] have been reported to markedly enhance cerium retention and membrane durability. However, these approaches often rely on strong coordination or irreversible structural modification, which may perturb the delicate nanophase-separated ion-cluster morphology of PFSA membranes. In addition, the lack of systematic understanding of ligand–cerium interactions and their spatial distribution within the nanostructured membrane matrix has limited the rational optimization of these systems. As a result, cerium leaching, microstructural disruption, and processing complexity remain unresolved challenges.

From a materials design perspective, an effective cerium immobilization strategy should ideally combine (i) moderate coordination strength to regulate cerium mobility without forming rigid ionic crosslinks, (ii) non-covalent interactions to minimize permanent perturbation of polymer architecture, and (iii)

compatibility with the nanoconfined ion-cluster environment of PFSA membranes. Crown ether-based ligands, characterized by well-defined cavity sizes and tunable host–guest interactions, offer a promising platform to achieve such regulation at polymer nanointerfaces. Functionalized crown ethers may provide tunable coordination environments and secondary interaction sites, enabling controlled cerium confinement while minimizing disruption of proton-conducting nanodomains.

In this work, we employ 2-(hydroxymethyl)-15-crown-5-ether (HMCRE) as a model ligand to construct a crown ether-coordinated cerium complex and investigate its behavior within PFSA membranes. 2-(hydroxymethyl)-15-crown-5-ether was selected as a model ligand because it combines an oxygen-rich crown cavity for moderated Ce coordination with a hydroxymethyl group that may be capable of secondary hydrogen-bonding interactions with PFSA side chains. This structure provides an opportunity to balance Ce confinement and nanophase compatibility without covalent modification of the PFSA backbone. By integrating coordination interactions with secondary hydrogen bonding, this system enables regulated cerium confinement at polymer nanointerfaces. The effects of such nanointerface-mediated interactions on membrane microstructure, ion transport, and chemical durability are systematically examined. Through combined experimental characterization and density functional theory (DFT) analysis, this study aims to elucidate how coordination-driven nanoconfinement and confined microenvironments govern cerium retention and radical scavenging behavior, providing new insights into the design of durable ionomer membranes.

2 Experimental

2.1 Materials

Cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.99%) and HMCRE (98%) were supplied by Alfa Aesar. Cerium oxide (CeO_2 , 20–50 nm), hydrogen peroxide solution (H_2O_2 , 30 wt.%), 6-carboxyfluorescein, and iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, > 99%) were acquired from Adamas Reagent Co., Ltd. and used as received for further characterization. N,N-Dimethylformamide (DMF, analytical reagent (AR)) and sulfuric acid (H_2SO_4 , 98 wt.%) were supplied by Sinopharm Chemical Reagent Co., Ltd. The PFSA ionomer (Nafion D520, EW 1100) was acquired from Chemours Chemicals Co., Ltd. Deionized water was employed for the whole experiment.

2.2 Synthesis of Ce/HMCRE Complex

Due to the intense metal ion complexation ability of HMCRE, Ce/HMCRE complexes were formed by simply mixing Ce salt with HMCRE at equal mole ratios in an aqueous solution. Specifically, an aqueous solution containing HMCRE (0.560 g, 4 mmol) was slowly added to an aqueous solution containing $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1.736 g, 4 mmol). After stirring overnight, the suspension was filtered and subsequently freeze-dried for 24 h to obtain the ultimate Ce/HMCRE coordination complex.

2.3 Preparation of hybrid membranes

A homogeneous Nafion solution was obtained by replacing water and n-propanol in D520 with DMF by rotary evaporation [38]. Ce/HMCRE was initially added to DMF and stirred for 6 h to

achieve uniform dispersion. The Ce/HMCRE solution was then mixed with the Nafion solution to continue stirring overnight to obtain a homogeneous mixture. The same procedure was employed to prepare Nafion mixtures containing $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and HMCRE for comparison. The relative values of Ce^{3+} or HMCRE to $[-\text{SO}_3\text{H}]$ were fixed as 3 mol% to identify the amount of Ce/HMCRE, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and HMCRE added. The PEMs were fabricated by the flow-casting method. A homogeneous Nafion mixture was cast onto a flat glass substrate and maintained at 50 °C overnight. Subsequently, an annealing process was conducted at 150 °C for 2 h. Ultimately, the prepared membranes were immersed in a 1 M H_2SO_4 solution at 80 °C for 0.5 h, followed by a deionized water rinse at 80 °C for 0.5 h. The membranes maintained a consistent thickness of $20 \pm 1 \mu\text{m}$.

3 Results and discussion

3.1 Chemical structure and morphological characterization

To elucidate the molecular configuration of the Ce/HMCRE complex and its interaction with the PFSA ionomer, we first examined the coordination structure formed between Ce^{3+} ions and

the tailored HMCRE ligand. As illustrated in Fig. 1(a), mixing Ce/HMCRE with PFSA is expected to yield antioxidant ionomers in which Ce^{3+} is preferentially confined within the crown ether cavity rather than remaining freely dispersed in the polymer matrix, suggesting a coordination-enabled confinement at polymer nanointerfaces. Several possible coordination configurations have been proposed for Ce^{3+} interacting with crown ether ligands [39]. Among them, the hydrated $\text{Ce}(\text{H}_2\text{O})_9^{3+}$ -based sunrise-type configuration (denoted as Ce/HMCRE-3 in Fig. S1 and Table S1 in the Electronic Supplementary Material (ESM)), exhibiting the most negative binding free energy $-23.42 \text{ kcal}\cdot\text{mol}^{-1}$, is the most thermodynamically favorable. This suggests that Ce^{3+} ions preferentially occupy the electron-rich cavity of HMCRE, where the oxygen atoms serve as primary coordination sites.

The Fourier transform infrared (FTIR) spectra provide further experimental evidence for this coordination environment. As shown in Fig. 1(b), the characteristic C–O–C stretching band of HMCRE at 1120 cm^{-1} splits and shifts to 1112 and 1069 cm^{-1} after complexation with Ce^{3+} . Such peak splitting and slight blueshift are indicative of electron-density redistribution induced by metal–ligand coordination, where lone pair electrons on oxygen atoms interact with vacant orbitals of Ce^{3+} [40, 41].

X-ray photoelectron spectroscopy (XPS) characterization further

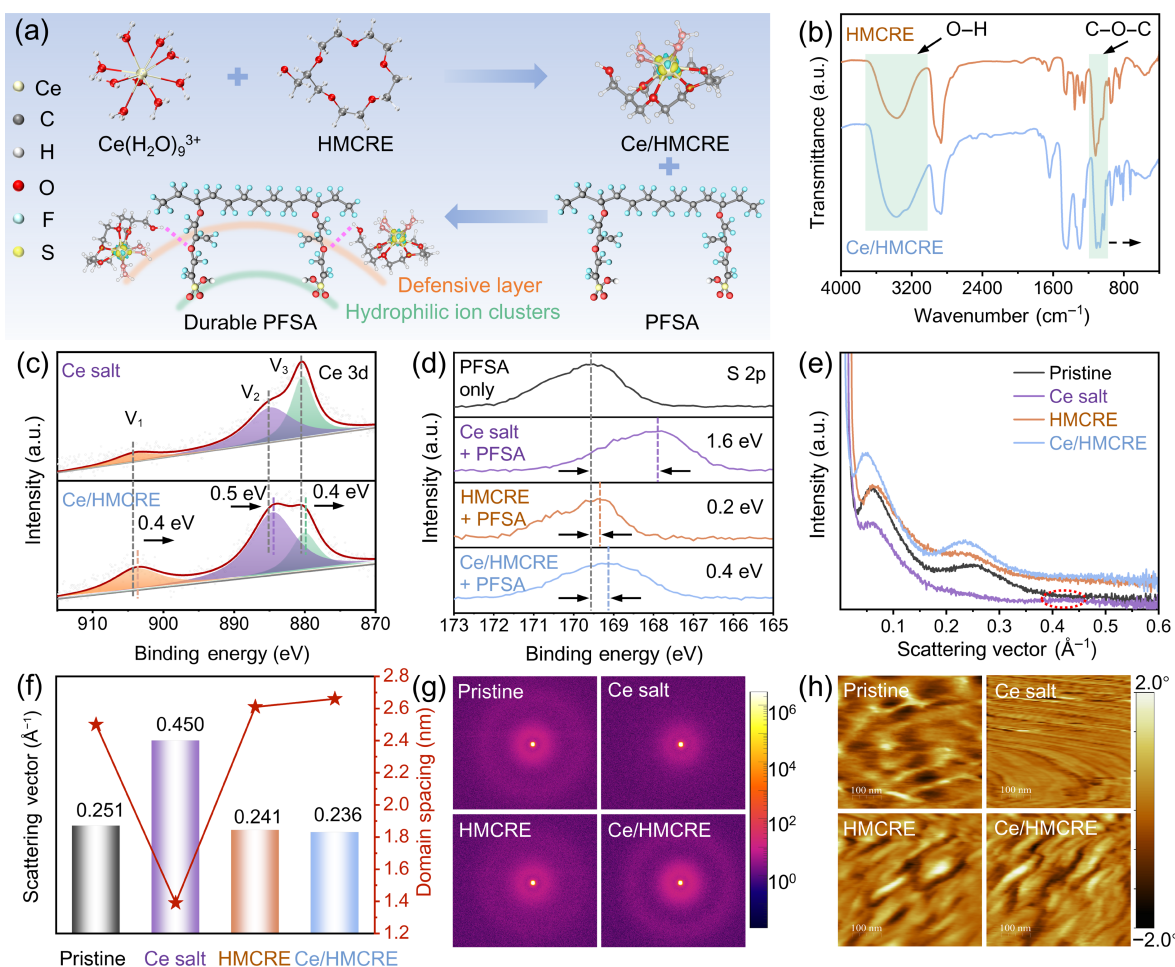


Figure 1 Synthesis and structural identification. (a) Schematic of the synthetic route of Ce/HMCRE and its interaction in PFSA. Light yellow, gray, white, red, yellow, and light blue balls represent Ce, C, H, O, S, and F. The Ce/HMCRE model is presented as a differential charge density plot. The yellow regions denote accumulation, while cyan regions indicate electron depletion. Isosurfaces were extracted at a charge density level of 0.01 (or -0.01) e^-/bohr^3 . (b) FTIR spectra and (c) Ce 3d XPS spectra of HMCRE and Ce/HMCRE complex. (d) S 2p spectra of pure PFSA and PFSA-containing Ce salt, HMCRE, and Ce/HMCRE. (e) SAXS patterns, (f) scattering vector of ionomer peak and corresponding ion cluster domain spacing, (g) 2D SAXS images, and (h) AFM phase images.

reveals the electronic interaction between Ce and the ligand. As shown in Fig. 1(c), The Ce 3d spectra of Ce salt and Ce/HMCRE can be deconvoluted into three peaks labeled V_1 , V_2 , and V_3 , all of them belonging to the valence state of Ce^{3+} (V_1 , V_2 , and V_3 are the valence forms 1, 2, and 3 of Ce^{3+} , respectively), consistent with Refs. [42–44]. The multiple Ce 3d peaks originate from spin-orbit splitting and multiplet final-state features of Ce^{3+} , rather than from different Ce species. These peaks collectively confirm the presence of Ce^{3+} centers in Ce/HMCRE. Notably, Ce/HMCRE displays a small but meaningful negative binding-energy shift relative to Ce salt, implying increased electron density around the Ce center after coordination. This trend aligns with FTIR observations, confirming electron donation from the ligand to Ce^{3+} . To probe nanointerface interaction between additives and the PFSA ionomer, S 2p and O 1s spectra were collected for PFSA mixed with Ce/HMCRE, HMCRE, and Ce salt. As shown in Fig. 1(d), all mixtures exhibit negative shifts relative to pristine PFSA, reflecting interaction with $-SO_3^-$ groups. However, the magnitude of the shift follows the order: Ce salt (1.6 eV) > Ce/HMCRE (0.4 eV) > HMCRE (0.2 eV). This trend clearly indicates that HMCRE coordination effectively shields Ce^{3+} from direct electrostatic interactions with $-SO_3^-$ groups, thereby minimizing perturbation to proton-conducting sites [38]. The slight S 2p shift induced by HMCRE indicates there is still a weak interaction between HMCRE and the PFSA side-chain environment, possibly through hydrogen bonding or dipole interactions. The O 1s spectra (Fig. S2 in the ESM) show a consistent trend, with Ce/HMCRE exhibiting weaker C–O signals than HMCRE, attributable to electron redistribution within the coordinated complex [45, 46].

Small-angle X-ray scattering (SAXS) analysis was performed to examine changes in ionic-cluster nanostructure. As shown in Fig. 1(e), two distinct scattering peaks appear: The low scattering vector (q) peak ($\sim 0.06 \text{ \AA}^{-1}$) corresponds to inter-crystalline spacing within the polymer matrix (“matrix knee”), while the high q peak ($\sim 0.25 \text{ \AA}^{-1}$) originates from the average spacing of hydrophilic ion-cluster nanodomains within the nanophase-separated structure. Based on Bragg’s law, the corresponding ion-cluster spacing (Fig. 1(f)) slightly increases for HMCRE-based (2.61 nm) and Ce/HMCRE-based membranes (2.66 nm), which can be attributed to water accommodation within the hydrophilic ligand-associated nanodomains. In contrast, Ce salt-based membranes exhibit a significantly reduced spacing (1.39 nm), attributed to strong electrostatic cross-linking between Ce^{3+} and $-SO_3^-$ groups that induce local collapse of ion-cluster nanodomains (Fig. S3 in the ESM). The two-dimensional (2D) SAXS patterns reveal diffuse scattering rings for pristine, HMCRE-based, and Ce/HMCRE-based membranes (Fig. 1(g)), indicative of well-preserved phase separation, whereas the Ce salt-based membrane shows more attenuated patterns.

Atomic force microscopy (AFM) phase images further visualize these nano-structural differences (Fig. 1(h)). In all samples, the dark regions correspond to hydrophilic ion-conducting nanodomains, while the bright regions represent the fluorinated hydrophobic matrix. Ce salt-based PEMs exhibit blurred and poorly connected ion-cluster nanodomains, consistent with aggregation of Ce^{3+} around multiple $-SO_3^-$ groups, which disrupts nanochannel connectivity and increases transport tortuosity [47]. In contrast, both HMCRE-based and Ce/HMCRE-based PEMs maintain well-defined and continuous ion-conducting nanodomains, comparable to pristine PFSA, indicating that ligand-assisted coordination minimizes perturbation of nanophase-separated structures.

3.2 Physical and chemical properties of the obtained membranes

Water plays an essential role in PFSA membranes by serving as both a proton carrier and a medium for forming hydrogen bonding networks within ion-cluster nanochannels. As shown in Fig. 2(a), the water uptake and dimensional swelling of the membranes exhibit distinct variations depending on the type of additive incorporated. The Ce/HMCRE-based and HMCRE-based PEMs exhibit slightly higher water uptake than pristine membranes, which may be associated with the hydrophilic nature of the HMCRE ligand. This observation is consistent with the presence of ether and hydroxyl groups on the ligand, which interact favorably with water molecules and help maintain hydration within ion-cluster nanodomains. In contrast, the Ce salt-based PEM shows reduced water uptake, consistent with stronger interactions between free Ce^{3+} and $-SO_3^-$ groups that may limit the availability of water binding sites within nanoconfined ionic regions.

The proton conductivity of the membranes (Fig. 2(b)) reflects the combined effects of ion-cluster nanostructure and hydration behavior. At low relative humidity (< 60% RH), both Ce/HMCRE-based and HMCRE-based membranes exhibit slightly enhanced proton conductivity compared with pristine PFSA. This improvement can be attributed to the water-retentive nature of HMCRE, which sustains hydration within ion-cluster nanochannels and provides additional hydrogen-bonding sites that facilitate proton hopping. As humidity increases, the pristine membrane achieves the highest conductivity, benefitting from its relatively open ion-cluster nanostructure and larger amount of free water [48]. In contrast, Ce salt-based membranes consistently show the lowest conductivity across all humidities because the strong Ce^{3+} – SO_3^- interactions hinder proton dissociation and restrict proton transport within nanoconfined ionic pathways.

The activation energies (E_a) derived from Arrhenius fitting (Fig. 2(c)) provide further insight into proton transport. The Ce salt-based membranes exhibit the highest E_a ($16.5 \text{ kJ}\cdot\text{mol}^{-1}$), indicating a more hindered conduction process associated with the restricted proton mobility of protons in the presence of strongly bound Ce^{3+} . In comparison, the E_a values for the Ce/HMCRE-based and HMCRE-based membranes (12.8 and $13.4 \text{ kJ}\cdot\text{mol}^{-1}$, respectively) closely resemble that of pristine PFSA ($12.3 \text{ kJ}\cdot\text{mol}^{-1}$), which is consistent with their relatively preserved ionic-cluster connectivity as observed in SAXS and AFM analyses.

Mechanical properties provide additional insight into the impact of additives [49]. In Fig. 2(d), the tensile strengths of Ce/HMCRE-based and HMCRE-based PEMs are 17.8 and 17.3 MPa , respectively, slightly surpassing the pristine membranes’ value of 16.4 MPa . In contrast, Ce salt-based membranes exhibit noticeable reductions in both tensile strength and elongation at break. This deterioration likely arises from the strong coordination of free Ce^{3+} with multiple $-SO_3^-$ groups, which perturbs native polymer–polymer interactions and leads to a more heterogeneous microstructure with less efficient stress transfer [50].

Thermal properties further reflect these structural effects. The Ce salt-based membrane shows a lower glass transition temperature (T_g) relative to pristine PFSA (Fig. S4 in the ESM), consistent with the disturbed ion-cluster nanostructure observed in AFM. HMCRE-based and Ce/HMCRE-based membranes exhibit slightly elevated T_g values, likely due to hydrogen-bonding interactions between the hydroxymethyl group of HMCRE and ether oxygen atoms in the PFSA side chains, which restrict chain mobility within

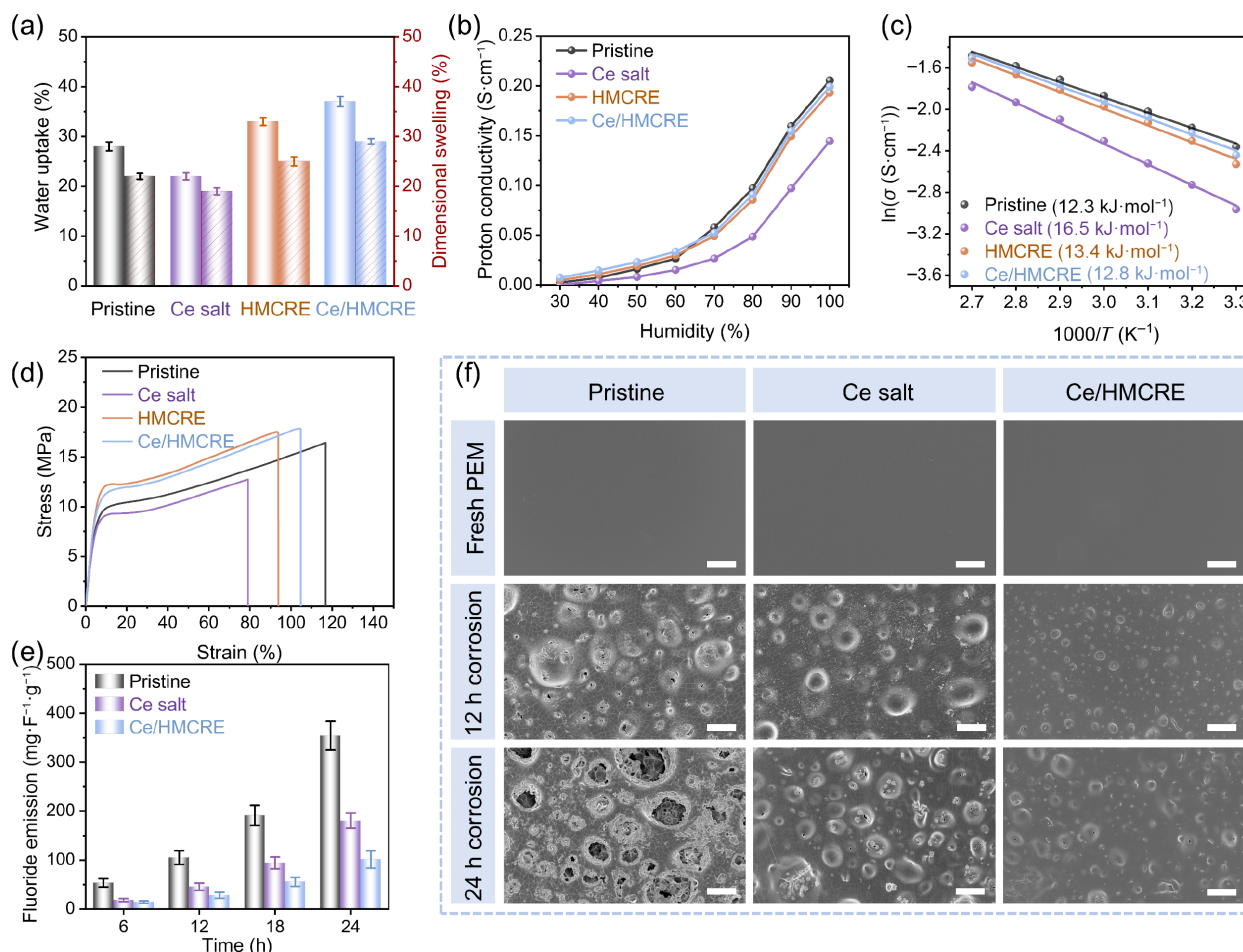


Figure 2 Characterization of physical and chemical properties for obtained membranes. (a) Water uptake and dimensional swelling. (b) Humidity-dependent proton conductivity at 80 °C. (c) Arrhenius plots of proton conductivity and corresponding activation energies under 100% RH. (d) Strain–stress curves. (e) Fluoride release of the pristine, Ce salt-based, and Ce/HMCRE-based membranes. (f) SEM images of the pristine, Ce salt-based, and Ce/HMCRE-based membranes before and after free radical corrosion. The scale bar above is 100 μm.

nanoconfined regions. Thermogravimetric analysis (TGA) results (Fig. S5 in the ESM) show that free Ce³⁺ accelerates the thermal degradation of PFSA owing to its Lewis-acid catalytic activity [51], whereas coordination with HMCRE mitigates this effect, resulting in improved thermal stability for Ce/HMCRE-based membranes.

Chemical durability was further evaluated through the Fenton test (Fig. 2(e)). Pristine PFSA undergoes significant degradation, as indicated by high fluoride release (354.1 mg·F⁻¹·g⁻¹) after 24 h. Both Ce salt-based and Ce/HMCRE-based membranes display reduced fluoride release, confirming the radical scavenging function of cerium species. Notably, Ce/HMCRE-based membranes exhibit the lowest fluoride release (101.4 mg·F⁻¹·g⁻¹), substantially below that of Ce salt-based membranes (180.4 mg·F⁻¹·g⁻¹). This significant reduction suggests that Ce/HMCRE provides more sustained radical-scavenging activity than free Ce³⁺ under aggressive oxidative conditions. To further distinguish the role of HMCRE from that of Ce coordination, the Fenton test was also conducted for the HMCRE-only membrane (Fig. S6 in the ESM). The HMCRE-only membrane shows only limited reduction in fluoride release compared with pristine PFSA, whereas the Ce/HMCRE-based membrane exhibits substantially lower fluoride release. This result confirms that the improved oxidative stability mainly arises from the coordinated Ce/HMCRE complex rather than from the intrinsic radical-scavenging ability of HMCRE alone. Moreover, to

directly evaluate ·OH scavenging behavior, a fluorescence-based radical-probe experiment was performed. The decay of fluorescence intensity (*I*) of 6-carboxyfluorescein dye in the presence of the Fenton reagent was monitored with and without radical scavengers to semi-quantitatively verify the high radical scavenging activity of radical scavenger observed in the aqueous Fenton test. Figure S7 in the ESM shows the ratio of fluorescence intensity after the addition of Fenton's reagent with and without scavengers to the fluorescence intensity of the un-degraded dye (*I*₀). The results show that the Ce/HMCRE system shows higher retention of *I* compared to pristine, Ce salt and HMCRE, indicating more effective ·OH removal.

The scanning electron microscopy (SEM) images reveal that all membranes show smooth and uniform surfaces prior to Fenton exposure (Fig. 2(f)). After 12 h, the pristine and Ce salt-based membranes develop numerous bubble-like surface defects, which subsequently rupture into cavities after 24 h, indicating pronounced chemical degradation. In contrast, the Ce/HMCRE-based membrane exhibits only uniformly distributed small bubbles after 12 h and maintains an intact surface morphology without observable rupture even after 24 h of exposure. These results demonstrate that the Ce/HMCRE effectively suppresses degradation of polymer, consistent with the reduced fluoride release observed in the chemical durability tests.

3.3 PEMFC performance and durability

The fuel cell performance of pristine, Ce salt-based, HMCRE-based, and Ce/HMCRE-based PEMs was evaluated using a single-cell configuration (Fig. 3(a)). As shown in Fig. 3(b), the current densities at 0.6 V ($j_{0.6V}$) are 2174, 1712, 2011, and 2073 mA·cm⁻² for pristine, Ce salt-based, HMCRE-based, and Ce/HMCRE-based PEMs, respectively. The corresponding maximum power densities are 1.332 W·cm⁻² for pristine PFSA, 1.248 W·cm⁻² for HMCRE-based, and 1.281 W·cm⁻² for Ce/HMCRE-based membranes, which remain higher than that of the Ce salt-based membrane (1.058 W·cm⁻²). These results indicate that incorporating HMCRE or Ce/HMCRE does not markedly compromise the electrochemical performance, consistent with the preserved ion-cluster nanostructure that supports efficient proton transport within nanochannels. Hydrogen crossover values (Fig. 3(c)) fall within 1.41–1.58 mA·cm⁻² for all membranes, with the Ce salt-based membrane showing the highest value, likely due to disruption of ion-cluster nanostructure caused by strong Ce³⁺-polymer interactions [27].

To assess durability, an *in-situ* harsh accelerated degradation test (ADT) was conducted. As shown in Fig. 3(d), the open-circuit voltage (OCV) of the pristine membrane decreases substantially from 0.983 to 0.798 V within 150 h (1.23 mV·h⁻¹), consistent with radical-induced chemical degradation. The Ce salt-based membrane shows a moderate OCV decline (0.71 mV·h⁻¹). In contrast, the Ce/HMCRE-based membrane exhibits a smaller OCV

loss of 67.5 mV, corresponding to a lower decay rate of 0.45 mV·h⁻¹, indicating significantly improved voltage stability under oxidative conditions. Hydrogen crossover at 0.4 V ($j_{H_2@0.4V}$), a key indicator of membrane integrity, increases sharply for pristine PFSA (from 1.45 to 12.56 mA·cm⁻²), reflecting severe oxidative damage (Fig. 3(e) and Fig. S8 in the ESM). The Ce salt-based membrane shows a more moderate increase (from 1.58 to 6.02 mA·cm⁻²), whereas the Ce/HMCRE-based membrane displays only a slight rise (from 1.47 to 2.41 mA·cm⁻²), indicating that nano-structural integrity is largely preserved.

After 150 h of ADT, the $j_{0.6V}$ of the Ce/HMCRE-based membrane remains at 1652 mA·cm⁻² (Fig. S9 in the ESM), outperforming both pristine PFSA (1054 mA·cm⁻²) and the Ce salt-based membrane (1113 mA·cm⁻²). The retention of maximum power density (P_{Max}) follows the order Ce/HMCRE-based (83.4%) > Ce salt-based (74.6%) > pristine (55.4%). Cross-sectional SEM images (Fig. S10 in the ESM) show notable thinning of the pristine membrane (76.0% thickness retention), whereas Ce/HMCRE-based PEMs retain 91.5% of their initial thickness, compared with 85.5% for Ce salt-based PEMs. These results collectively indicate that Ce/HMCRE effectively stabilizes membrane nanostructure and mitigates degradation under harsh oxidative conditions (Fig. 3(f)). The OCV decay rate achieved by Ce/HMCRE-based PEMs compares favorably with values reported in Refs. [11, 15, 29, 30, 38, 42, 52–58] (Fig. 3(g)), further demonstrating the effectiveness of nanointerface-regulated cerium confinement in improving PEM durability.

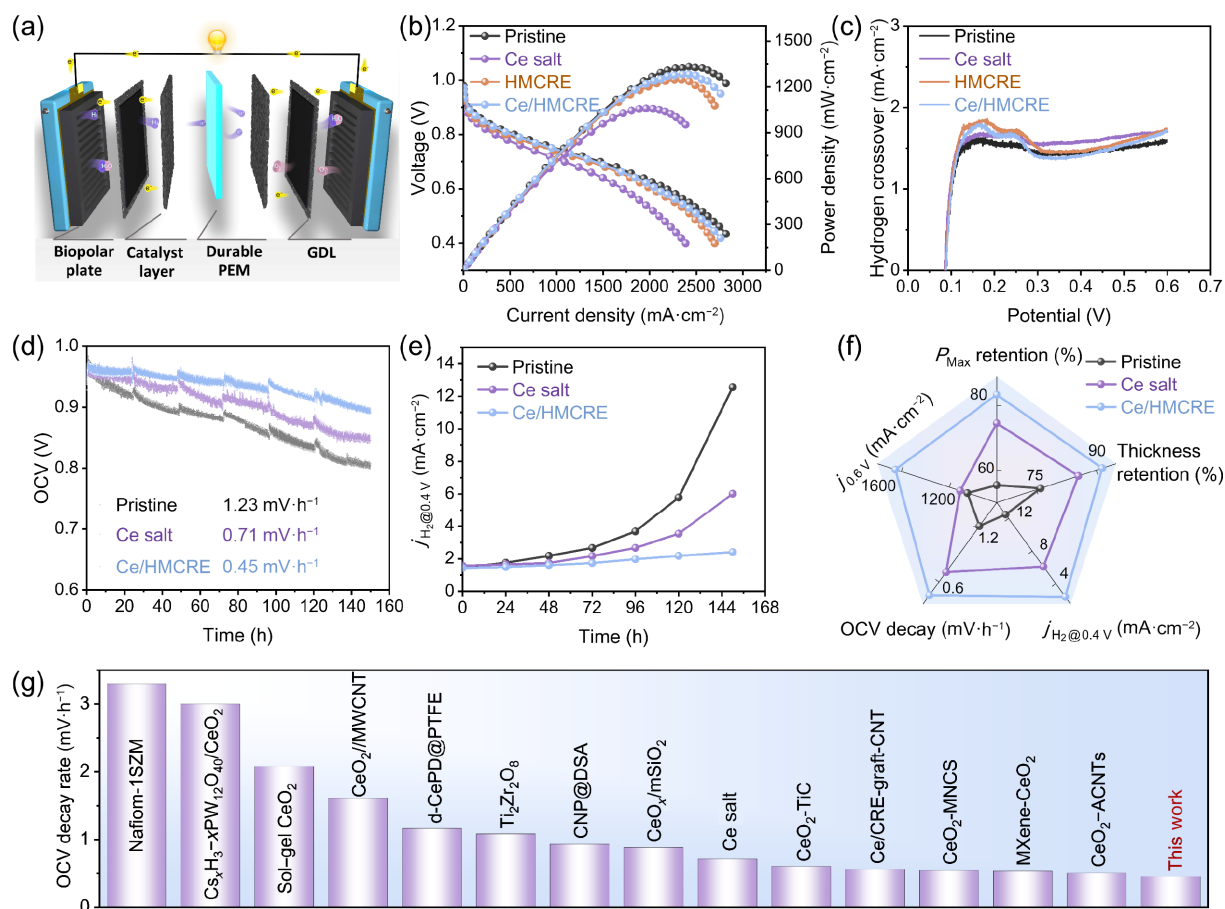


Figure 3 PEMFC performance and durability of PEMs. (a) Schematic illustration of PEMFC. (b) Current–voltage (*I*–*V*) polarization curves and power density curves. (c) Hydrogen crossover curves measured by linear scanning voltammetry. (d) OCV decay during ADT. (e) Variation of hydrogen crossover current during ADT. (f) Comparison of $j_{0.6V}$, P_{Max} retention, thickness retention, $j_{H_2@0.4V}$, and OCV decay after ADT. (g) Comparison of OCV decay rates with other reported work.

3.4 Insight into the stabilizing mechanism of Ce/HMCRE organometallic complex

The preceding results suggest that the enhanced durability of the Ce/HMCRE-based PEMs originates from regulation of cerium behavior within a nanoconfined coordination environment. To understand how crown ether coordination influences the redox properties of Ce species, DFT calculations were performed to analyze the electrostatic potential (ESP) distribution and charge density differences of HMCRE and Ce/HMCRE (Fig. 4(a)). The HMCRE molecule exhibits a negative potential cavity within the crown ether ring, which facilitates complexation with Ce^{3+} . Upon complexation, the negative ESP around the oxygen atoms decreases, indicating partial electron donation from the ligand to the metal center [59]. This electron redistribution is further supported by the charge density difference map (Fig. S1 in the ESM), which shows electron depletion around the oxygen atoms and accumulation near the Ce center. The charge-density difference results indicate that electron redistribution mainly occurs between Ce^{3+} and the crown ether oxygen atoms, confirming that the crown cavity serves as the primary coordination environment. In contrast, the hydroxymethyl group does not significantly participate in Ce coordination but rather may potentially serve as a secondary hydrogen-bonding site for interfacial anchoring with PFSA side chains.

The influence of this coordination-induced electronic modulation on redox behavior was further evaluated by calculating

the $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox potentials ($E_{\text{Ce}^{3+}/\text{Ce}^{4+}}$), as shown in Fig. 4(b) and Table S2 in the ESM. The Ce/HMCRE complex exhibits a lower calculated redox potential ($E = 2.779$ V) than hydrated $\text{Ce}(\text{H}_2\text{O})_9^{3+}$ (3.097 V), indicating that the coordinated Ce^{3+} center is more readily oxidized within the crown ether nanoconfined coordination environment and potentially more reactive toward radical scavenging [60, 61]. The lower calculated oxidation potential indicates enhanced redox accessibility rather than irreversible Ce^{4+} formation. In the radical-scavenging cycle, Ce^{4+} is oxidized by radicals, and Ce^{4+} can be reduced back to Ce^{3+} by peroxides (e.g., H_2O_2 and $\cdot\text{OOH}$). The improved ADT stability and reduced fluoride release suggest that Ce/HMCRE maintains an effective redox cycle under oxidative conditions.

This computational trend is consistent with cyclic voltammetry (CV) measurements, where Ce/HMCRE shows a higher electrochemical response toward $\cdot\text{OH}$ ($1.516 \text{ mA}\cdot\text{mg}_{\text{Ce}}^{-1}$) compared with free Ce^{3+} ($1.008 \text{ mA}\cdot\text{mg}_{\text{Ce}}^{-1}$) and commercial CeO_2 nanoparticles ($0.875 \text{ mA}\cdot\text{mg}_{\text{Ce}}^{-1}$) (Figs. 4(c) and 4(d)). Herein, the electrochemical response refers to the Ce-mass-normalized current response caused by the redox interaction between Ce-based species and $\cdot\text{OH}$ radicals generated from the Fenton reaction. The agreement between DFT predictions and CV results supports the interpretation that ligand coordination enhances the radical-scavenging reactivity of Ce.

In addition to enhanced redox reactivity, the residence time of Ce within the membrane critically influences long-term durability. Because the HMCRE ligand contains a hydroxymethyl group

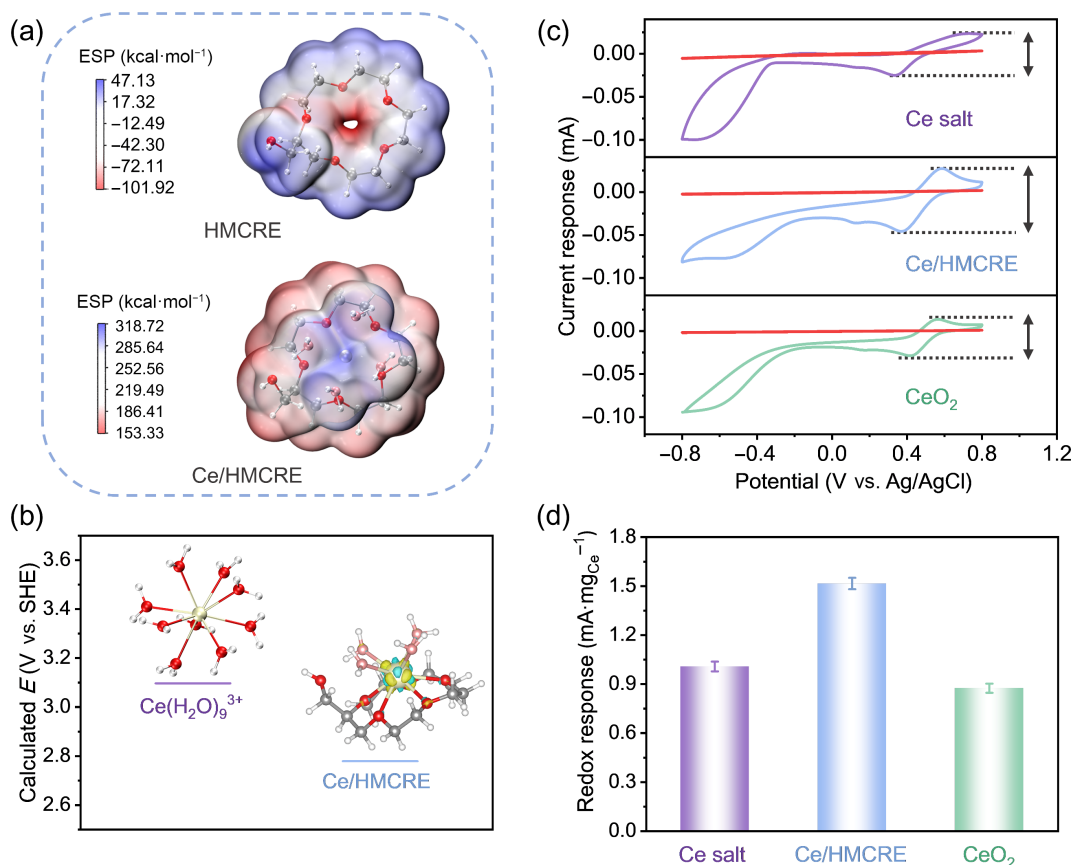


Figure 4 Electronic structure modulation and redox behavior of Ce/HMCRE complex. (a) ESP of HMCRE and Ce/HMCRE. (b) DFT-calculated E values of $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox reaction of $\text{Ce}(\text{H}_2\text{O})_9^{3+}$ and Ce/HMCRE complexes. (c) CV curves of the Ce salt, Ce/HMCRE, and CeO_2 -modified glassy carbon electrode toward 10 mM of $\cdot\text{OH}$ from the Fenton reaction. (d) Calculated redox response obtained with Ce salt, Ce/HMCRE, and CeO_2 toward 10 mM of $\cdot\text{OH}$ (Fenton reaction) normalized per mass of cerium on the electrode.

capable of hydrogen bonding, we evaluated the possible interactions between Ce/HMCRE and representative ether oxygen sites on PFSA side chains. DFT calculations indicate that such interactions favor adsorption at polymer nanointerfaces, with site 2 showing the most favorable binding energy ($-2.36 \text{ kcal}\cdot\text{mol}^{-1}$) (Fig. 5(a) and Table S3 in the ESM). To experimentally evaluate this effect, Ce retention was quantified by energy dispersive X-ray spectroscopy (EDS) after immersion in sulfuric acid for 240 h. The Ce/S molar ratio of Ce/HMCRE-based membranes remains at 2.05 mol%, compared with only 0.43 mol% for Ce salt-based membranes (Figs. 5(b) and 5(c)), corresponding to a 3.76 fold increase in Ce retention.

Moreover, the Ce distribution on the cross-sections of MEAs for Ce salt-based and Ce/HMCRE-based membranes was analyzed by elemental linear mapping after ADT (Fig. S11 in the ESM). The signal intensity of Ce in the Ce salt-based membrane was highest at the boundary between the catalytic layer and the PEM and gradually decreased along the catalytic layer to the microporous

layer, indicating the migration of Ce ions from the PEM. However, the Ce/HMCRE-based membrane retains a more stable Ce distribution after ADT compared with the Ce salt-based membrane, supporting the effectiveness of ligand-assisted confinement under fuel-cell operating conditions. This enhanced stability is consistent with hydrogen-bond-assisted anchoring predicted by DFT. Importantly, the preferred adsorption sites are located away from primary ion-cluster nanodomains, suggesting that Ce/HMCRE is anchored at polymer nanointerfaces without significantly interfering with proton-conducting pathways. This spatial selectivity is consistent with SAXS and AFM results, where Ce/HMCRE-based membranes maintain well-defined nanophase-separated structures. Although direct atomic-scale visualization of Ce species at PFSA nanointerfaces remains challenging, the combined XPS, SAXS, AFM, DFT, and SEM-EDS results consistently support a nanointerface-regulated confinement scenario. In this model, Ce/HMCRE is stabilized through crown ether coordination and secondary hydrogen-bonding interactions

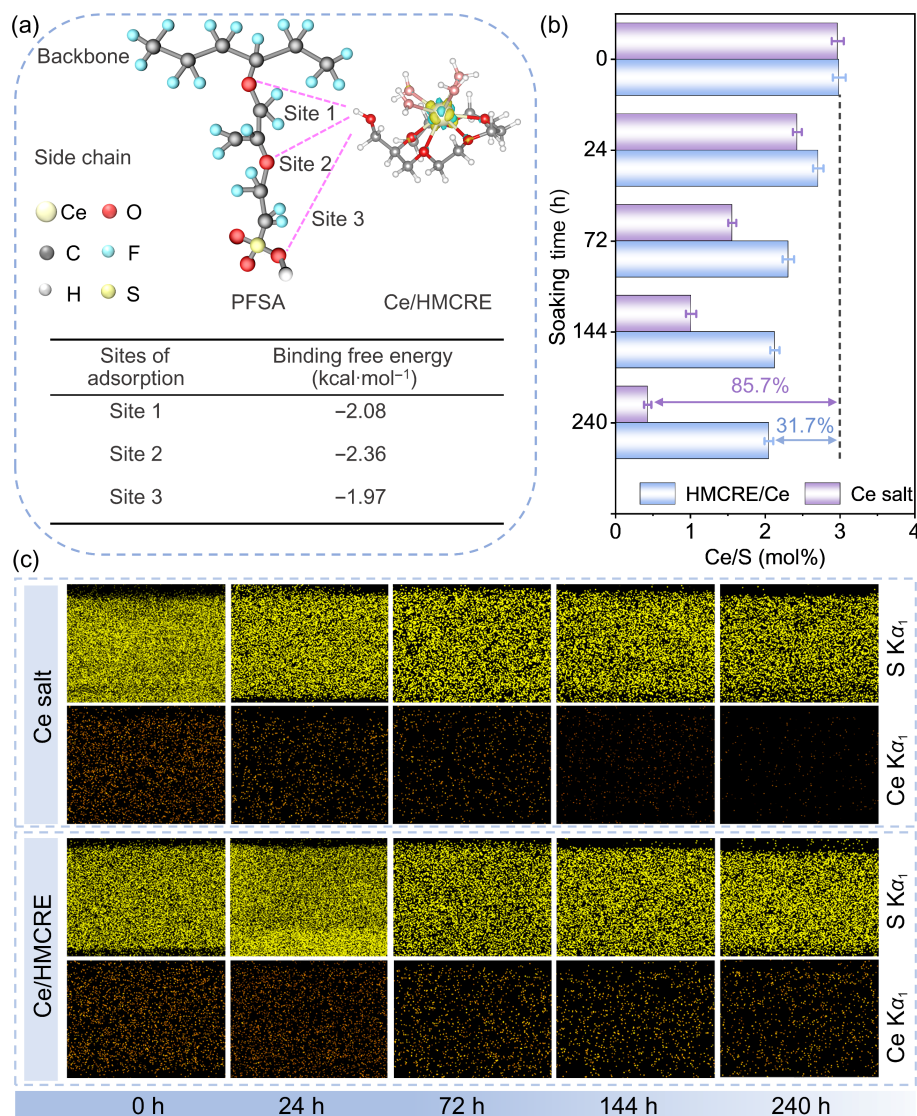


Figure 5 Hydrogen-bonding interactions and cerium retention behavior in PFSA membranes. (a) The potential sites (Sites 1, 2, and 3) for Ce/HMCRE adsorption on PFSA and the corresponding binding free energy (listed in the table). The purple dotted lines represent hydrogen bonds. Light yellow, gray, white, red, yellow, and light blue balls represent Ce, C, H, O, S, and F. (b) Ce/S molar ratio. (c) SEM-EDS mapping images of Ce salt-based and Ce/HMCRE-based membranes after soaking in sulfuric acid solution for different durations.

with PFSA side-chain ether sites, thereby reducing direct intrusion into sulfonate-rich ion-cluster domains.

In summary, coordination between Ce^{3+} and the HMCRE ligand modulates the electronic structure of the metal center and facilitates redox reactions within a nanoconfined environment, while hydrogen-bond-mediated interfacial interactions enhance cerium retention and minimize perturbation of ion-cluster nanostructure. The combination of these effects provides a mechanistic basis for the improved chemical durability of Ce/HMCRE-based PEMs.

4 Conclusions

In this work, we developed a ligand-coordinated Ce/HMCRE complex as a stabilized free-radical scavenger for improving the chemical durability of proton exchange membranes. The crown ether-assisted coordination confines Ce^{3+} within a nanoconfined environment and reduces undesirable interactions with sulfonic acid groups. Simultaneously, hydrogen-bonding interactions between the hydroxymethyl group of HMCRE and PFSA side chains provide interfacial anchoring at polymer nanointerfaces, suppressing cerium migration while minimizing perturbation of ion-cluster nanostructure. DFT calculations indicate that ligand coordination redistributes electron density around the Ce center and lowers the oxidation barrier from Ce^{3+} to Ce^{4+} , which is consistent with the enhanced radical-scavenging activity observed experimentally. As a result, Ce/HMCRE-based membranes exhibit a 3.76 fold increase in cerium retention and significantly improved resistance to chemical degradation compared with membranes containing free Ce^{3+} . These molecular and nanointerface-level advantages translate into superior fuel-cell durability, as evidenced by an ultralow OCV decay rate of $0.45 \text{ mV}\cdot\text{h}^{-1}$ and 83.4% peak power density retention after 150 h of accelerated degradation testing. Overall, this work highlights the importance of nanointerface regulation and confined microenvironments in controlling redox-active species within ionomer membranes, providing a promising strategy for the design of durable electrochemical energy materials.

Electronic Supplementary Material: Supplementary material (details of the experimental, DFT-optimized structure of Ce/HMCRE, XPS measurements, SAXS measurements, differential scanning calorimetry (DSC) and TGA measurements, fluorescence measurements, hydrogen crossover measurements, SEM measurements, and detailed parameters for calculating the binding free energies) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908896>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

S. Q. Z.: Writing – original draft, validation, formal analysis, visualization, conceptualization, writing – review & editing. Z. Q. Y.: Investigation. Y. C. L.: Methodology. R. W.: Visualization. H. L.: Formal analysis. J. P. S.: Data curation. T. T.: Investigation. L. Z.: Methodology. S. H. C.: Supervision. H. L. T.: Funding acquisition, project administration, supervision, writing – review and editing. All the authors have approved the final manuscript.

Use of AI statement

None.

References

- [1] Zhang, F.; Zu, B. F.; Wang, B. W.; Qin, Z. K.; Yao, J. Q.; Wang, Z. X.; Fan, L. H.; Jiao, K. Developing long-durability proton-exchange membrane fuel cells. *Joule* **2025**, *9*, 101853.
- [2] Zhang, H. H.; Fan, Y. P.; Guan, S. Y.; Cui, W. G.; Zhang, M. C.; Li, Z. L.; Dou, Y. H.; Yang, J. R.; Zhuang, Z. C.; Yuan, Z. L. et al. Research progress on Ti-based materials for MgH_2 hydrogen storage systems. *Compos. Funct. Mater.* **2025**, *1*, 20250201.
- [3] Wang, S. W.; Wang, L. G.; Zhou, X. D.; Fang, J. J.; Deng, C.; Wang, D. S. Design principles of single-atom catalysts anchored over porous materials for green catalysis and conversion. *Nano Res.* **2025**, *18*, 94907137.
- [4] Wang, Y.; Ma, F. Y.; Zhang, G. Q.; Zhang, J. W.; Zhao, H.; Dong, Y. M.; Wang, D. S. Precise synthesis of dual atom sites for electrocatalysis. *Nano Res.* **2024**, *17*, 9397–9427.
- [5] Zhang, Y. F.; He, Z. D.; Yang, C.; Cao, P. P.; Ma, Q.; Liu, H.; Heng, X. Y.; Gu, T. H.; Shi, J. Q.; Mu, X. Q. et al. Interfacial microenvironment regulation strategies for industrial-scale hydrogen evolution. *EnergyChem* **2026**, *8*, 100189.
- [6] Zhang, M. Y.; Luo, X.; Zhou, D. Y.; Wang, S. C.; Chen, S. R.; Du, Y. P.; Zhuang, Z. C.; Yang, J. R.; Zhu, W.; Liu, S. L. et al. Multiscale manipulation of functional imperfection atomic interfaces. *Acc. Chem. Res.* **2026**, *59*, 322–336.
- [7] Liu, H.; Zhang, Y.; Liu, Z. Y.; Wang, S. C.; Mu, X. Q.; Zhang, Q. H.; Cao, W.; Liu, S. L.; Wang, D. S.; Dai, Z. H. Grain boundary-driven synergistic dual-mechanism catalysis in RuO_2 for enhancing acidic oxygen evolution reaction activity and stability. *J. Am. Chem. Soc.* **2025**, *147*, 44141–44151.
- [8] Liu, F. H.; Kim, I. S.; Miyatake, K. Proton-conductive aromatic membranes reinforced with poly(vinylidene fluoride) nanofibers for high-performance durable fuel cells. *Sci. Adv.* **2023**, *9*, eadg9057.
- [9] Liu, B. H.; Liu, Q.; Pang, Y.; Duan, Y. T.; Zhao, C. J. Antioxidant sulfide-linked polymer membrane with inherent microporosity enables fuel cells to achieve outstanding power density and durability over a wide temperature range. *Adv. Funct. Mater.* **2025**, *35*, 2408291.
- [10] Yang, X. C.; Feng, Z. M.; Alshurafa, M.; Yu, M.; Foster, A. B.; Zhai, H.; Yuan, T. M.; Xiao, Y. H.; D'Agostino, C.; Ai, L. et al. Durable proton exchange membrane based on polymers of intrinsic microporosity for fuel cells. *Adv. Mater.* **2025**, *37*, 2419534.
- [11] Duan, Y. T.; Pang, Y.; Liu, B. H.; Wu, L. M.; Hu, X. Y.; Li, Q. J.; Zhao, C. J. Synergistic utilization of a CeO_2 -anchored bifunctionalized metal–organic framework in a polymer nanocomposite toward achieving high power density and durability of PEMFC. *ACS Sustainable Chem. Eng.* **2023**, *11*, 5270–5283.
- [12] Zhai, H.; Chen, J. N.; Meng, C.; Yang, X. C.; Zhou, Z. Y.; Ai, L.; Li,

- J. S.; Miller, T. S.; Perez-Page, M.; Holmes, S. M. Nanofiber membranes for enhanced performance and optimization of proton exchange membrane fuel cells. *Sci. Adv.* **2025**, *11*, eadw5747.
- [13] Guan, P. P.; Zou, Y. C.; Zhang, M.; Zhong, W. K.; Xu, J. Q.; Lei, J. L.; Ding, H.; Feng, W.; Liu, F.; Zhang, Y. M. High-temperature low-humidity proton exchange membrane with “stream-reservoir” ionic channels for high-power-density fuel cells. *Sci. Adv.* **2023**, *9*, eadh1386.
- [14] Liu, B. X.; Liao, Y. C.; Zhao, S. Q.; Li, Y.; Zhang, Z.; Zhang, J. J.; Song, X. Y.; Zeng, P.; Chai, M. R.; Ye, Q. et al. The proton exchange membrane with a nanosilica-phosphate-quaternary ammonium type proton transport structure for cross-temperature range applications. *J. Membr. Sci.* **2025**, *724*, 123991.
- [15] Zhao, S. Q.; Wang, R.; Tian, T.; Liu, H.; Zhang, H. N.; Tang, H. L. Self-assembly-cooperating *in situ* construction of MXene-CeO₂ as hybrid membrane coating for durable and high-performance proton exchange membrane fuel cell. *ACS Sustainable Chem. Eng.* **2022**, *10*, 4269–4278.
- [16] Trogisch, N.; Du, F. M.; Albert, A.; Eichel, R. A. Modelling the chemical degradation of PFSA membranes in proton exchange membrane fuel cells-effect of low relative humidity on the degradation of the sulfonic acid group. *J. Electrochem. Soc.* **2025**, *172*, 074501.
- [17] Agarwal, T.; Adhikari, S.; Babu, S. K.; Prasad, A. K.; Advani, S. G.; Borup, R. L. Biosourced antioxidants for chemical durability enhancement of perfluorosulfonic acid membrane. *Adv. Funct. Mater.* **2024**, *34*, 2308856.
- [18] Theerthagiri, S.; Budi Rachman, I.; Shoriful Islam, M.; Park, J. Y.; Song, S. J. Ce-metal organic frameworks for enhanced chemical stability and durability of sulfonated polyether ether ketone for proton exchange membranes. *ACS Appl. Polym. Mater.* **2025**, *7*, 3954–3967.
- [19] Xu, Y.; Liang, X.; Shen, X. H.; Yu, W. S.; Yang, X. Q.; Li, Q. H.; Ge, X. L.; Wu, L.; Xu, T. W. *In situ* construction of ultra-thin PANI/CeO_x layer on proton exchange membrane for enhanced oxidation resistance in PEMFC. *J. Membr. Sci.* **2024**, *689*, 122167.
- [20] Zhao, S. Q.; Liao, Y. C.; Wang, R.; Li, Y.; Shuai, J. Q.; Wang, L. T.; Liu, B. X.; Chen, R.; Tian, T.; Zhang, H. N. et al. Phosphate-grafted polyethyleneimine-induced multifunctional cerium oxide as an antioxidant for simultaneously enhancing the proton conductivity and durability of proton exchange membranes. *Adv. Compos. Hybrid. Mater.* **2024**, *7*, 66.
- [21] Wang, Z. H.; Xu, K. W.; Xu, X. J.; Sun, Y. X.; Liu, G. C.; Liu, F.; Zhang, Y. M.; Wei, G.; Pei, S. P. Manganese(II)-genistein complex as an efficient radical scavenger for fuel cells and investigation of its antioxidant mechanism. *Int. J. Hydrogen Energy* **2025**, *103*, 111–118.
- [22] Hossain, S. M.; Patnaik, P.; Bhat, S. D.; Chatterjee, U. Synergistic radical scavenging and multifaceted membrane properties: Comparative evaluation of CeMO_x (M = Zr, Mn, Zn) bimetallic oxide embedded sPEEK membranes for hydrogen fuel cells. *J. Membr. Sci.* **2025**, *728*, 124159.
- [23] Coms, F. D.; Liu, H.; Owejan, J. E. Mitigation of perfluorosulfonic acid membrane chemical degradation using cerium and manganese ions. *ECS Trans.* **2008**, *16*, 1735–1747.
- [24] Kwon, T.; Lim, Y.; Cho, J.; Lawler, R.; Min, B. J.; Goddard, W. A.; Jang, S. S.; Kim, J. Y. Antioxidant technology for durability enhancement in polymer electrolyte membranes for fuel cell applications. *Mater. Today* **2022**, *58*, 135–163.
- [25] Baker, A. M.; Crothers, A. R.; Chintam, K.; Luo, X. Y.; Weber, A. Z.; Borup, R. L.; Kusoglu, A. Morphology and transport of multivalent cation-exchanged ionomer membranes using perfluorosulfonic acid-Ce²⁺ as a model system. *ACS Appl. Polym. Mater.* **2020**, *2*, 3642–3656.
- [26] Yuk, S.; Lee, D. W.; Song, K. Y.; Choi, S.; Lee, D. H.; Doo, G.; Hyun, J.; Kwon, J.; Kim, J. Y.; Kim, H. T. Detrimental effect of Ce⁴⁺ ion on the Pt/C catalyst in polymer electrolyte membrane fuel cells. *J. Power Sources* **2020**, *448*, 227447.
- [27] Zhao, S. Q.; Liao, Y. C.; Wang, R.; Liu, G. L.; Zhang, H. N.; Tang, H. L. Polyphenol synergistic cerium oxide surface engineering constructed core-shell nanostructures as antioxidants for durable and high-performance proton exchange membrane fuel cells. *Chem. Eng. J.* **2023**, *472*, 144804.
- [28] Park, J.; Park, Y.; Kim, D. Chemical stability enhancement of crown ether grafted sulfonated poly(arylene ether ketone) fuel cell membrane by cerium ion fixation. *J. Polym. Sci., Part A: Polym. Chem.* **2019**, *57*, 101–109.
- [29] Yoon, K. R.; Lee, K. A.; Jo, S.; Yook, S. H.; Lee, K. Y.; Kim, I. D.; Kim, J. Y. Mussel-inspired polydopamine-treated reinforced composite membranes with self-supported CeO_x radical scavengers for highly stable PEM fuel cells. *Adv. Funct. Mater.* **2019**, *29*, 1806929.
- [30] Oh, K. H.; Goo, Y.; Kim, M.; Park, J.; Nam, K. W.; Kim, H. Enhanced chemical durability of polymer electrolyte membrane fuel cells by crown ether grafted carbon nanotube. *J. Alloys Compd.* **2022**, *928*, 167227.
- [31] Hossain, S. M.; Patnaik, P.; Bhat, S. D.; Chatterjee, U. Surface engineered CeMnO_x@DHNS core-shell nanostructures as multifunctional additives for highly durable proton exchange membranes. *Chem. Eng. J.* **2025**, *525*, 170365.
- [32] Tu, Z. Q.; He, X.; Du, X.; Li, W. X.; Wang, D. H.; Fang, W.; Zhang, H. J.; Chen, H.; Zhao, L.; Wang, C. Missing-linker defects of Ce–UiO-66 for enhanced radical scavenging efficiency and proton conductivity in proton exchange membrane fuel cells. *Chem. Eng. J.* **2025**, *505*, 159357.
- [33] Kwon, T.; Park, S. H.; Min, B. J.; Park, S.; Ramadhani, S.; Lim, Y.; Jang, S. S.; Jeong, H.; Son, H. J.; Kim, J. Y. Ce(III)-based coordination-complex-based efficient radical scavenger for exceptional durability enhancement of polymer application in proton-exchange membrane fuel cells and organic photovoltaics. *Adv. Energy Sustain. Res.* **2022**, *3*, 2200011.
- [34] Park, J.; Kim, D. Effect of cerium/18-crown-6-ether coordination complex OH quencher on the properties of sulfonated poly(ether ether ketone) fuel cell electrolyte membranes. *J. Membr. Sci.* **2014**, *469*, 238–244.
- [35] Agarwal, T.; Sievert, A. C.; Komini Babu, S.; Adhikari, S.; Park, E. J.; Prasad, A. K.; Advani, S. G.; Hopkins, T. E.; Park, A. M.; Kim, Y. S. et al. Enhancing durability of polymer electrolyte membrane using cation size selective agents. *J. Power Sources* **2023**, *580*, 233362.
- [36] Lu, Z. R.; Yang, Z. R.; Li, X. H.; Chang, Z. W.; Jia, X. Y.; He, S. J.; Lin, J. Using quercetin to anchor a novel Ce-doped acid to enhance the performance and chemical stability of proton exchange membranes. *J. Membr. Sci.* **2026**, *742*, 125155.
- [37] Agarwal, T.; Matanovic, I.; Adhikari, S.; Park, E. J.; Komini Babu, S.; Kim, Y. S.; Tian, D.; Bae, C.; Morales-Collazo, O.; Brennecke, J. F. et al. Mitigating cerium migration for perfluorosulfonic acid membranes using organic ligands. *J. Power Sources* **2023**, *554*, 232320.
- [38] Wang, Z.; Tang, H. L.; Zhang, H. J.; Lei, M.; Chen, R.; Xiao, P.; Pan, M. Synthesis of Nafion/CeO₂ hybrid for chemically durable proton exchange membrane of fuel cell. *J. Membr. Sci.* **2012**, *421–422*, 201–210.
- [39] Steed, J. W. First- and second-sphere coordination chemistry of alkali metal crown ether complexes. *Coord. Chem. Rev.* **2001**, *215*, 171–221.
- [40] Yang, Q.; Sun, L. X.; Gao, W. T.; Zhu, Z. Y.; Gao, X.; Zhang, Q. G.; Zhu, A. M.; Liu, Q. L. Crown ether-based anion exchange membranes with highly efficient dual ion conducting pathways. *J. Colloid Interface Sci.* **2021**, *604*, 492–499.
- [41] Su, T. S.; Eickemeyer, F. T.; Hope, M. A.; Jahanbakhshi, F.; Mladenović, M.; Li, J.; Zhou, Z. W.; Mishra, A.; Yum, J. H.; Ren, D. et al. Crown ether modulation enables over 23% efficient formamidinium-based perovskite solar cells. *J. Am. Chem. Soc.* **2020**, *142*, 19980–19991.
- [42] Yook, S. H.; Kim, H. Y.; Kim, S. J.; Choi, S.; Kwon, T.; Cho, H.; Kim, J. M.; Yoon, K. R.; Jo, S.; Lee, S. Y. et al. Boosting

- antioxidation efficiency of nonstoichiometric CeO_x nanoparticles via surface passivation toward robust polymer electrolyte membrane fuel cells. *Chem. Eng. J.* **2022**, *432*, 134419.
- [43] Hu, B. T.; Sun, K. A.; Zhuang, Z. W.; Chen, Z.; Liu, S. J.; Cheong, W. C.; Chen, C.; Hu, M. Z.; Cao, X.; Ma, J. G. et al. Distinct crystal-facet-dependent behaviors for single-atom palladium-on-ceria catalysts: Enhanced stabilization and catalytic properties. *Adv. Mater.* **2022**, *34*, 2107721.
- [44] Pereira-Hernández, X. I.; DeLaRiva, A.; Muravev, V.; Kunwar, D.; Xiong, H. F.; Sudduth, B.; Engelhard, M.; Kovarik, L.; Hensen, E. J. M.; Wang, Y. et al. Tuning Pt–CeO₂ interactions by high-temperature vapor-phase synthesis for improved reducibility of lattice oxygen. *Nat. Commun.* **2019**, *10*, 1358.
- [45] Vo, D. C. T.; Nguyen, M. D. T.; Kim, D. Dual sulfonated poly(arylene ether ketone) membrane grafted with 15-crown-5-ether for enhanced proton conductivity and anti-oxidation stability. *Mol. Syst. Des. Eng.* **2019**, *4*, 901–911.
- [46] Yang, X. R.; Ma, L.; Wang, S. Q.; Hu, X. Y.; Li, B.; Li, W.; Wang, D. S.; Dai, Z. H. Electrochemiluminescence-based multiplex immunoassays for multianalyte bioanalysis: Signal encoding strategies and analytical perspectives. *Electrochem. Commun.* **2026**, *186*, 108130.
- [47] Mauritz, K. A.; Moore, R. B. State of understanding of Nafion. *Chem. Rev.* **2004**, *104*, 4535–4586.
- [48] Liao, Y. C.; Wang, R.; Zhao, S. Q.; Zhang, J. J.; Wu, S. H.; Liu, B. X.; Chen, R.; Tian, T.; Jin, H. Y.; Tang, H. L. Enhancing proton delocalization in non-sulfonated membranes through coupled electron-withdrawing groups for high-temperature fuel cells. *ACS Nano* **2025**, *19*, 40536–40546.
- [49] Yuan, H.; Chen, P. F.; Li, X.; Xu, X. X.; Qian, W.; Zhang, H. Z.; Wang, Z.; Fu, H. Q.; Wang, D. S.; He, D. P. Scalable fiber-skeleton-reinforced graphene-assembled films enabling wash-durable wearable heating. *Nano Res.* **2026**, *19*, 94908671.
- [50] Li, Y. X.; Liang, L.; Liu, C. P.; Li, Y.; Xing, W.; Sun, J. Q. Self-healing proton-exchange membranes composed of Nafion-poly(vinyl alcohol) complexes for durable direct methanol fuel cells. *Adv. Mater.* **2018**, *30*, 1707146.
- [51] Sun, L. Y.; Thrasher, J. S. Studies of the thermal behavior of Nafion® membranes treated with aluminum(III). *Polym. Degrad. Stab.* **2005**, *89*, 43–49.
- [52] Patel, H. A.; Mansor, N.; Gadipelli, S.; Brett, D. J. L.; Guo, Z. X. Superacidity in Nafion/MOF hybrid membranes retains water at low humidity to enhance proton conduction for fuel cells. *ACS Appl. Mater. Interfaces* **2016**, *8*, 30687–30691.
- [53] Zhao, D.; Yi, B. L.; Zhang, H. M.; Yu, H. M.; Wang, L.; Ma, Y. W.; Xing, D. M. Cesium substituted 12-tungstophosphoric (Cs_xH_{3–x}PW₁₂O₄₀) loaded on ceria-degradation mitigation in polymer electrolyte membranes. *J. Power Sources* **2009**, *190*, 301–306.
- [54] Kim, H.; Yook, S. H.; Kim, H. Y.; Choi, Y.; Lim, Y.; Hwang, Y.; Kim, J.; Lee, K. Y.; Jang, S. S.; Park, J. et al. Tailor-made charged catechol-based polymeric ligands to build robust fuel cells containing antioxidative nanoparticles. *Adv. Electron. Mater.* **2022**, *8*, 2200171.
- [55] Tsipoaka, M.; Aziz, M. A.; Park, J.; Shanmugam, S. Ti₂Zr₂O₈ nanotube as an additive in the fuel cell membrane and catalyst layer for improved low humidity operation. *J. Power Sources* **2021**, *509*, 230386.
- [56] Baker, A. M.; Wang, L.; Johnson, W. B.; Prasad, A. K.; Advani, S. G. Nafion membranes reinforced with ceria-coated multiwall carbon nanotubes for improved mechanical and chemical durability in polymer electrolyte membrane fuel cells. *J. Phys. Chem. C* **2014**, *118*, 26796–26802.
- [57] Vinothkannan, M.; Ramakrishnan, S.; Kim, A. R.; Lee, H. K.; Yoo, D. J. Ceria stabilized by titanium carbide as a sustainable filler in the Nafion matrix improves the mechanical integrity, electrochemical durability, and hydrogen impermeability of proton-exchange membrane fuel cells: Effects of the filler content. *ACS Appl. Mater. Interfaces* **2020**, *12*, 5704–5716.
- [58] Vinothkannan, M.; Hariprasad, R.; Ramakrishnan, S.; Kim, A. R.; Yoo, D. J. Potential bifunctional filler (CeO₂–ACNTs) for Nafion matrix toward extended electrochemical power density and durability in proton-exchange membrane fuel cells operating at reduced relative humidity. *ACS Sustainable Chem. Eng.* **2019**, *7*, 12847–12857.
- [59] Jing, Z. F.; Wang, G. G.; Zhou, Y. Q.; Pang, D. K.; Zhu, F. Y.; Liu, H. Y. Selectivity of 18-crown-6 ether to alkali ions by density functional theory and molecular dynamics simulation. *J. Mol. Liq.* **2020**, *311*, 113305.
- [60] Konezny, S. J.; Doherty, M. D.; Luca, O. R.; Crabtree, R. H.; Soloveichik, G. L.; Batista, V. S. Reduction of systematic uncertainty in DFT redox potentials of transition-metal complexes. *J. Phys. Chem. C* **2012**, *116*, 6349–6356.
- [61] Bogart, J. A.; Lewis, A. J.; Schelter, E. J. DFT study of the active site of the XoxF-type natural, cerium-dependent methanol dehydrogenase enzyme. *Chem.—Eur. J.* **2015**, *21*, 1743–1748.



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