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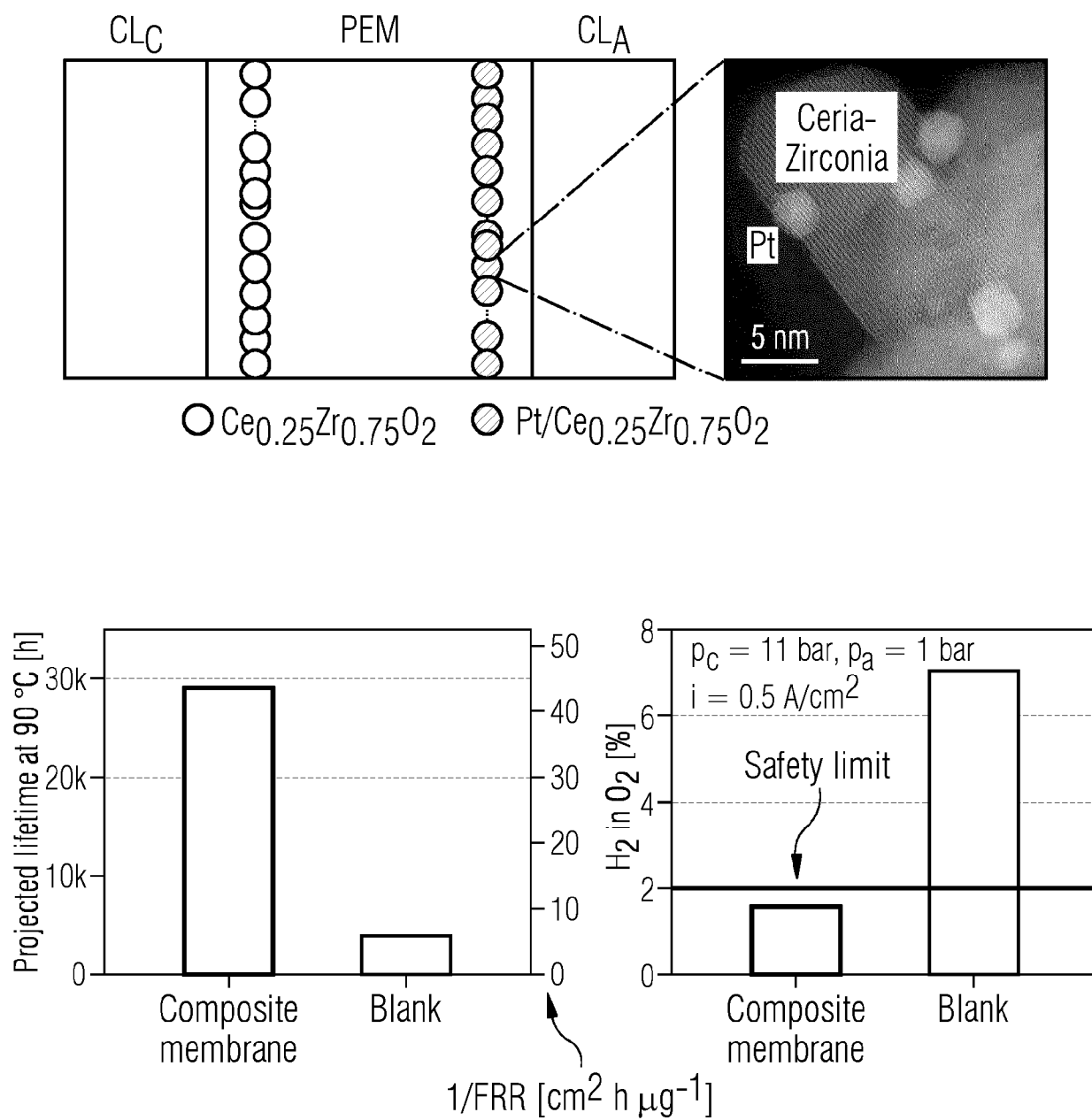
(54) **ELECTROCHEMICAL CELL COMPRISING A COMPOSITE PROTON EXCHANGE
MEMBRANES WITH INTERLAYER STRUCTURE**

(57) The development of more cost-effective and efficient proton exchange membrane (PEM) water electrolysis cells requires the use of thinner membranes with extended lifetimes and reduced gas crossover. The inventive approach to address these challenges involves the incorporation of radical scavengers to mitigate radical-induced ionomer degradation, along with gas recombination catalysts to promote the conversion of crossover hydrogen and oxygen to water inside the PEM. Each of the two catalyst types has its distinct chemical reaction characteristics, to which the design of the composite membrane is tailored through rational considerations. In various embodiments of the present invention, the positioning effects of $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ and Pt interlayers in composite membranes for their respective roles in radical scavenging and gas recombination were investigated. Results reveal that placing a radical scavenger interlayer near the cathode notably reduces the ionomer degradation rate, compared to its placement near the anode, evidenced by a $61\% \pm 7\%$ reduction in fluoride release rate. This is likely due to reactive oxygen species in the cell being predominantly generated at the cathode, which

is closer to the radical scavenger interlayer in the former case. The Ce content in cerium-zirconium oxide was further optimized using an ex-situ Fenton test, with $\text{Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$ demonstrating the highest radical scavenging activity. The Pt interlayer is confirmed to be more effective when positioned near the anode, exhibiting a 1.7-fold decrease in H_2 in $\text{O}_2\%$ compared to its positioning near the cathode, owing to a higher yield of the recombination reaction. The Pt interlayer, however, was found to induce additional ionomer degradation, and was replaced by a bi-functional catalyst $\text{Pt/Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$ interlayer. Consequently, this composite membrane configuration with a $\text{Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$ interlayer near the cathode and a $\text{Pt/Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$ interlayer near the anode yields the lowest rates of both ionomer degradation and hydrogen crossover among the configurations tested, demonstrating a projected membrane lifetime 7.4 times longer and a H_2 in $\text{O}_2\%$ 4.4 times lower than blank membranes without any functional catalyst particle interlayers. This composite membrane is therefore promising for applications in next-generation PEM water electrolysis cells.

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Figure 6



Description

[0001] The present invention relates to an electrochemical cell comprising a composite proton exchange membranes with interlayer structure.

[0002] Proton exchange membrane (PEM) water electrolysis is an anticipated core technology to produce hydrogen from renewable energy sources for power-to-X processes. Performance, cost and durability are widely considered as the three main challenges to the advancement of this technology. Enhancing the durability of PEM water electrolysis cells is crucial for reducing system costs and improving the economic competitiveness of the produced hydrogen. In the literature, stack lifetimes ranging from 60,000 to 100,000 hours have been reported, with projections anticipating an increase to over 125,000 hours by 2050. Among the factors influencing cell durability, chemical degradation of the membrane plays an important role, and is of particular relevance when thin membranes of $\sim 50 \mu\text{m}$ thickness or less are employed.

[0003] The irreversible chemical membrane degradation is typically driven by reactive oxygen species (ROS) that are generated on catalytic surfaces due to gas crossover. These ROS include hydrogen peroxide (H_2O_2) and its associated radicals, such as hydroxyl ($\text{HO}^\cdot$) and hydroperoxyl ($\text{HOO}^\cdot$) radicals. The radicals attack the polymer structure, leading to chain scission, and loss of ion-exchange groups and other structural constituents, resulting in membrane thinning and reduced ionic conductivity. In the case of perfluorosulfonic acid (PFSA)-based membranes, such as Nafion, the release of fluoride is detected in the cell effluent water, serving as an indicator of the polymer degradation.

[0004] It is generally accepted that this degradation primarily occurs near the cathode side, although a comprehensive understanding remains to be elucidated. Chandresis et al. developed a one-dimensional model addressing the degradation mechanism, involving the formation of H_2O_2 at the cathode as a result of oxygen crossover, followed by the generation of radicals via Fenton reactions. Experimental measurements of the fluoride release rate (FRR) supported the model, demonstrating higher FRR values at the cathode compared to the anode. This conclusion aligns with the observations made by Fouda-Onana et al. and Frensch et al.

[0005] It is thought that H_2O_2 is produced both chemically via the reaction of crossover hydrogen and oxygen gases on platinum (Pt) surfaces accompanied by radical formation, and electrochemically through a two-electron pathway at the cathode under low-potential conditions. H_2O_2 possesses a diffusion length on the order of millimeters to centimeters, allowing it to traverse the membrane. During its diffusion, H_2O_2 can decompose to form radicals, either uncatalyzed or catalyzed by certain metal ions.

[0006] An effective strategy for mitigating membrane chemical degradation is to incorporate a radical scavenger, such as a cerium (Ce)-based catalyst. It reacts with ROS while maintaining a dynamic equilibrium of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couple. Although Ce-based radical scavengers have been extensively studied in PEM fuel cell research, their application in PEM water electrolysis remains relatively limited to date. Current reports mainly describe the homogenous incorporation of the catalyst inside the membrane. However, since the membrane degradation predominantly takes place near the cathode, such a homogenous distribution may not represent the most efficient or optimal placement of the radical scavenger.

[0007] Furthermore, another obstacle in the development of PEM water electrolysis cells with thinner membranes is the increased hydrogen crossover. Recombination catalysts, such as Pt, have been employed to reduce the rate of crossover hydrogen reaching the anode side. Klose et al. proposed an ideal placement of the recombination catalyst layer within the membrane, taking into account the partial pressures and effective diffusion coefficients of hydrogen and oxygen in water under a set of given conditions. Specifically, in a typical PEM water electrolysis cell operating at 80°C - where the cathode H_2 chamber is usually pressurized while the anode O_2 chamber is maintained at ambient pressure - the optimal location for the recombination layer is near the anode side. Nevertheless, incorporating Pt as a recombination catalyst was found to exacerbate ionomer degradation, likely due to its role in catalyzing additional radical formation.

[0008] Summarizing the objective of the present invention, it was the goal to provide an electrochemical cell, in particular a water electrolysis cell, having a high capability of an effective radical scavenger and of reducing the hydrogen cross-over when using thin membranes.

[0009] According to the present invention, the positioning of the antioxidant, such as a Ce-based radical scavenger, as an interlayer near the cathode side is considered to ensure effectiveness of the radical scavenger by targeting the region close to the highest ROS concentration. The impact of radical scavenger positioning on mitigating membrane degradation has been largely overlooked in the literature so far, and thus, the present invention clearly advances the edge of the technology known so far.

[0010] Further, according to the present invention, the challenge of hydrogen cross-over is now tackled by a gas recombination catalyst, such as a $\text{Pt/Ce}_x\text{Zr}_{1-x}\text{O}_2$ bi-functional catalyst as a replacement for pure Pt, thereby achieving to concurrently mitigate hydrogen crossover and ionomer degradation. Building on the novel application of this bi-functional catalyst and informed by the optimal placement, the present invention preferably positions a gas recombination catalyst layer, such as a $\text{Pt/Ce}_x\text{Zr}_{1-x}\text{O}_2$ interlayer, near the anode side of the membrane, representing an unexplored approach in addressing the problem.

[0011] These objectives have been achieved according to the present invention by an electrochemical cell comprising a

catalyst coated membrane, i.e. for use in water electrolysis, wherein:

i) the membrane is a cation exchange membrane (CEM), in particular a proton exchange membrane (PEM), or an anion exchange membrane (AEM), in particular a hydroxide exchange membrane (HEM);

ii) said membrane having a thickness below 100 μm , preferably below 75 μm , more preferably below 50 μm ; and

iii) said membrane comprises an antioxidant (AO) and a gas recombination catalyst (GRC) in the form of micro and/or nanoparticles, preferably in form of a layer of antioxidant particles and a layer of gas recombination catalyst particles that are placed within the membrane close to the cathode side and the anode side respectively.

[0012] Advantageous embodiment of the present invention can be realized, when:

i) the antioxidant is an oxide of the type $\text{Ce}_{1-x-y-z}\text{M}_1\text{xM}_2\text{yM}_3\text{zO}_{2-d}$ comprising cerium as a redox-active transition metal, wherein M1 is one or more transition metals, M2 is one or more lanthanide metals, M3 is one of more noble or heavy metal, with $0 < x, y, z < 1$ and $2-d$ expresses the oxygen stoichiometry with $-0.5 < d < 0.5$;

ii) the oxide is of the type cerium oxide (CeO_{2-d}), cerium-zirconium oxide ($\text{Ce}_x\text{Zr}_{1-x}\text{O}_{2-d}$), cerium-gadolinium oxide ($\text{Ce}_x\text{Gd}_{1-x}\text{O}_{2-d}$), preferably: $\text{Ce}_x\text{Zr}_{1-x}\text{O}_{2-d}$ with $0.1 \leq x \leq 0.75$ and more preferably $0.2 \leq x \leq 0.5$, or the oxide is a metal organic framework (MOF) with Ce(III)/Ce(IV) as metal center, such as Ce-MOF-808;

iii) the gas recombination catalyst is:

a) a noble metal black, preferably Pt or Pd or an alloy of Pt and Pd, and/or

b) a noble metal, as described in a), supported on the antioxidant, preferably supported on $\text{Ce}_x\text{Zr}_{1-x}\text{O}_{2-d}$, such as Pt supported on $\text{Ce}_x\text{Zr}_{1-x}\text{O}_{2-d}$ (Pt- $\text{Ce}_x\text{Zr}_{1-x}\text{O}_{2-d}$) with a Pt content with respect to the oxide of preferably 1 to 20 wt-% and more preferably 2 to 10 wt-%, and/or

c) a noble metal, as described in a), inserted into the cavity of a MOF type antioxidant;

iv) said membrane is a proton exchange membrane of the perfluoroalkylsulfonic acid (PFSA) type, for example Nafion[™] (Chemours), Fumapem[®] and Fumasep[®] (Fumatech) or Aquivion[®] (Syensqo) or a proton exchange membrane of the hydrocarbon type, for example Pemion[™] (Ionomr) or an AEM, for example PiperION[®] (Versogen), Aemion[™] (Ionomr), Aemion+[™] (Ionomr), Duraion[®] (Creavis), Durion[™] (Xergy), Fumasep[®] (Fumatech), Sustainion[®] (Dioxide Materials);

v) the antioxidant particles are mixed with the same type of ionomer, optionally with a different equivalent weight, in dispersed form, that the membrane is made of and the resulting slurry is deposited onto the cathode side of the membrane by one or more of:

a) coating

b) printing

c) spraying

d) decal transfer,

wherein an antioxidant (AO) loading ranges from 0.01 to 2 mgAO/cm², more preferably 0.05 to 0.2 mgAO/cm², with a layer thickness of <10 μm , and wherein a further layer of the pure ionomer is added by one of the aforementioned methods with a thickness of less than 10 μm ; or

the antioxidant particles are incorporated into a cathode catalyst layer comprising an electrocatalyst for the hydrogen evolution reaction (HER), for example Pt/carbon, with a preferable load of the antioxidant (AO) in the range from 0.01 to 2 mgAO/cm², more preferably 0.05 to 0.2 mgAO/cm², and wherein the HER catalyst is a Pt/carbon catalyst, and the Pt loading of the cathode catalyst layer is preferably between 0.010 and 0.40 mgPt/cm², more preferably between 0.025 and 0.10 mgPt/cm²;

vi) the gas recombination catalyst particles are mixed with the same type of ionomer, in dispersed form, that the membrane is made of, and the resulting slurry is deposited onto the anode side of the membrane, by one or more of a) coating, b) printing, c) spraying and/or d) decal transfer, wherein a load of the gas recombination catalyst in terms of its noble metal content ranges from 0.001 to 0.1 mg(noble metal)/cm², more preferably 0.02 to 0.05 mg(noble metal)/cm², with a layer thickness below 10 μm and wherein a further layer of the pure ionomer is added by one of afore-mentioned methods with a thickness of less than 10 μm ;

vii) the catalyst coated membrane (CCM) is prepared by coating an anode and cathode catalyst layer onto the composite membrane comprising a layer of the gas recombination catalyst particles near the anode side of the membrane and a layer of the antioxidant particles near the cathode side of the membrane, unless the antioxidant particles are incorporated into the cathode catalyst layer;

viii) the composition of the anode catalyst layer comprises a catalyst for the oxygen evolution reaction (OER), such as IrOx, IrOx supported on TiO₂, IrOx supported on another oxide; or IrRuOx, IrRuOx supported on oxide; or, in the case of AEMWE, any oxide containing transition metals, such as NiFe layered double hydroxide (LDH)-based electro-catalyst, and an ionomer, which optionally is of the same type as the ionomer constituting the membrane, or of a different class of ionomer;

ix) the composition of the cathode catalyst layer comprises a catalyst for the hydrogen evolution reaction (HER), such as Pt black or Pt supported on carbon (Pt/C), or Pd black or Pd supported on carbon (Pd/C), or an alloy black containing Pt or Pd or both, or a carbon supported catalyst containing Pt or Pd or both, and an ionomer, which optionally is of the same type as the ionomer constituting the membrane, or of a different class of ionomer;

x) for the deposition process, an ink is formed from the respective catalyst and the respective ionomer using a solvent to obtain a slurry or paste, wherein the solvent is an organic solvent, water, or a mixture thereof;

xi) the anode and the cathode catalyst layer are deposited by one of more of a) coating, b) printing, c) spraying and/or d) decal transfer; and/or

xii) the catalyst coated membrane CCM is assembled into a water electrolyzer cell with the addition of the following components:

- a) a carbon-based gas diffusion layer (GDL) on the cathode side
- b) a titanium based porous transport layer (PTL) on the anode side
- c) optionally a sub-gasket for edge protection; and
- d) suitable seals and gaskets.

[0013] Preferred embodiments of the present invention are hereinafter described in more detail with reference to the attached drawings which depict in:

Figure 1 schematically a representation of composite membrane configurations $Ce_{0.5}Zr_{0.5}O_2$ (an) and $Ce_{0.5}Zr_{0.5}O_2$ (ca) (a), fluoride release rates determined during 100-hour constant current tests (b), polarization curves and iR-free potentials (c), and the corresponding high-frequency resistances (d) for these two composite membrane configurations;

Figure 2 a cross-sectional SEM image of the catalyst coated membrane (CCM) containing $Ce_{0.5}Zr_{0.5}O_2$ (ca);

Figure 3 PXRD patterns of the synthesized $Ce_xZr_{1-x}O_2$ ($x = 0.25, 0.5$ and 0.75) (a), N₂ physisorption isotherms and surface areas calculated using the BET method (b), schematic illustration of the ex-situ Fenton test set-up⁴⁸ (c), and fluoride concentrations monitored during the ex-situ Fenton tests (d) for these synthesized cerium-zirconium oxides;

Figure 4 Schematic representation of composite membrane configurations $Ce_{0.25}Zr_{0.75}O_2$ (ca) - Pt (ca), $Ce_{0.25}Zr_{0.75}O_2$ (ca) - Pt (an) and $Ce_{0.25}Zr_{0.75}O_2$ (ca) - Pt/ $Ce_{0.25}Zr_{0.75}O_2$ (an) (a), fluoride release rates determined during 100-hour constant current tests (b), measured H₂ in O₂% in the current density range of 0.5-3 A/cm² (c), polarization curves and iR-free potentials (d) and the corresponding high-frequency resistances (e) for these composite membrane configurations;

Figure 5 HAADF-STEM images of the synthesized Pt/ $Ce_{0.25}Zr_{0.75}O_2$ (a,b), with the EDX spectrum (c) acquired from the selected area in the image (Cu signals originate from the Cu grid used). The PXRD pattern with Rietveld refinement is presented in (d); and

Figure 6 schematically the principle of an electrochemical cell comprising a composite proton exchange membranes with interlayer structures.

[0014] The electrochemical cell, for example designed as water electrolysis cell, is usually operated at a slightly increased temperature, typically between 50 and 120°C, by feeding water to the electrochemical cell on the anode side or the cathode side, or both, and a voltage of typically 1.4 V - 2.5 V per cell or a current of 0.1 A/cm² - 5 A/cm² is applied. The gas pressure on the cathode (H₂ side) is typically between ambient and 30 bar, the gas pressure on the anode (O₂ side) between ambient and 5 bar.

[0015] In the present application, the work for the creation of an advantageous catalyst coated membrane (CCM) having a high capability of an effective radical scavenger and of reducing the hydrogen cross-over when using thin membranes began with the effective positioning of a model radical scavenger, Ce_{0.5}Zr_{0.5}O₂, placing a spray-coated Ce_{0.5}Zr_{0.5}O₂ interlayer near either the anode or cathode within the membrane. The FRRs of the two composite membranes were monitored and compared over 100 hours of constant current measurements at 2 A/cm². The Ce content in Ce_xZr_{1-x}O₂ was further optimized for the highest radical scavenging capability using an ex-situ Fenton test, identifying Ce_{0.25}Zr_{0.75}O₂ as the optimal composition. This material was therefore placed near the cathode side, which had been determined as the more effective location for radical scavenger within the composite membrane. The positioning of a gas recombination catalyst interlayer, with Pt as a model material, was additionally evaluated for its role in reducing hydrogen crossover. Consistent with the literature, the Pt interlayer was found to be more effective near the anode under the experimental conditions. To address the additional ionomer degradation induced by the Pt interlayer, a bi-functional catalyst Pt/Ce_{0.25}Zr_{0.75}O₂ interlayer has been introduced as a substitute. Building on these findings, a composite membrane configuration featuring Ce_{0.25}Zr_{0.75}O₂ near the cathode and Pt/Ce_{0.25}Zr_{0.75}O₂ near the anode was exemplarily developed and examined, achieving concurrently an enhanced mitigation of ionomer degradation and hydrogen crossover.

Effective Positioning of Ce_{0.5}Zr_{0.5}O₂ Radical Scavenging Interlayer

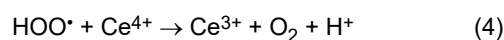
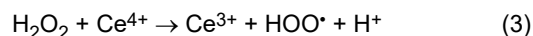
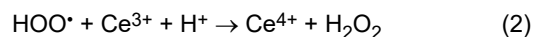
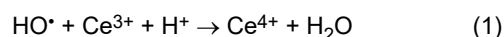
[0016] Two configurations of composite membranes were prepared, each incorporating a Ce_{0.5}Zr_{0.5}O₂ interlayer positioned either near the anode or near the cathode of a Nafion NR 212 membrane, as illustrated in Figure 1a. An ionomer layer was deposited over the Ce_{0.5}Zr_{0.5}O₂ interlayer to provide electrical insulation from the catalyst layer. The SEM cross-sectional image (Figure 2a), using Ce_{0.5}Zr_{0.5}O₂ (ca) as an example, shows a well-defined composite membrane structure, comprising a 47.6 ± 0.6 μm thick Nafion NR 212 membrane, a 7 ± 1 μm thick Ce_{0.5}Zr_{0.5}O₂ interlayer and a 5 ± 1 μm thick ionomer layer.

[0017] The radical scavenging effectiveness of the Ce_{0.5}Zr_{0.5}O₂ interlayer was evaluated in 100-hour constant current measurements at 2 A/cm², conducted at 90 °C under differential pressures ($p_c = 11$ bar and $p_a = 1$ bar). The fluoride release rates, calculated based on electro-osmotic drag water rates and fluoride concentrations in the cathode effluent water, are shown in Figure 1b. Blank measurements were performed using three membranes without any Ce_{0.5}Zr_{0.5}O₂ interlayers. Their averaged FRR, 0.17 ± 0.01 (μg·cm⁻²·h⁻¹), is represented by a solid horizontal line, with the error bar indicated by a grey-shaded region.

[0018] As mentioned, Figure 1 shows a schematic representation of composite membrane configurations Ce_{0.5}Zr_{0.5}O₂ (an) and Ce_{0.5}Zr_{0.5}O₂ (ca) (a), fluoride release rates determined during 100-hour constant current tests (b), polarization curves and iR-free potentials (c), and the corresponding high-frequency resistances (d) for these two composite membrane configurations.

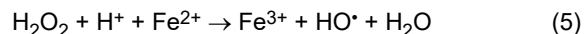
[0019] Figure 2 shows a cross-sectional SEM image of the catalyst coated membrane (CCM) containing Ce_{0.5}Zr_{0.5}O₂ (ca) (a) and the measured H₂ in O₂% for different membrane configurations at 0.5 A/cm² (b).

[0020] The results demonstrate that positioning the Ce_{0.5}Zr_{0.5}O₂ interlayer near the cathode effectively reduces the FRR compared to its placement near the anode - the latter exhibits an FRR similar to the blank level. The average FRR over the 100 hours for Ce_{0.5}Zr_{0.5}O₂ (an) is 0.18 ± 0.02 (μg·cm⁻²·h⁻¹), whereas for Ce_{0.5}Zr_{0.5}O₂ (ca) it is 0.07 ± 0.01 (μg·cm⁻²·h⁻¹), corresponding to a reduction of 61% ± 7%. Placing the radical scavenger closer to this region is beneficial in lowering the ROS concentrations, thereby improving the chemical stability of the membrane. Reactions involving ROS with the Ce⁴⁺/Ce³⁺ redox couple in cerium-zirconium oxide commonly include:



[0021] The oxidative strength of these ROS follows the order: HO[•] > H[•] > HOO[•] > H₂O₂. Notably, as HO[•] has a short diffusion length of ~40 nm in PFSA membranes, direct scavenging of HO[•] produced in the cathode catalyst layer by Ce_{0.5}Zr_{0.5}O₂ is unlikely due to the presence of an ionomer layer with a thickness in the range of 5 mm. Nevertheless, the

relatively stable ROS, H_2O_2 and $\text{HOO}^\bullet$, can diffuse from the cathode into the membrane towards the anode. Depending on the position of the $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ interlayer, they can be consumed by Ce^{4+} along their diffusion pathway, particularly for $\text{HOO}^\bullet$ whose diffusion length is $\sim 20\ \mu\text{m}$, shorter than the distance to the $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ interlayer when positioned near the anode. Scavenging these species closer to the cathode in a timely manner can, therefore, reduce the extent of membrane degradation. Furthermore, H_2O_2 and $\text{HOO}^\bullet$ participate in reactions that lead to the formation of $\text{HO}^\bullet$, such as the Fenton reaction involving H_2O_2 , as follows:



[0022] Here, iron ions could be present from feed water impurities. The decomposition of H_2O_2 can also be catalyzed by other multivalent metal ions, including Cu^{2+} and Ti^{3+} . These ions may arise from the corrosion of system tubing or cell components. A reduced H_2O_2 concentration near the cathode side, achieved using $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ in the configuration of $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (ca), mitigates subsequent $\text{HO}^\bullet$ formation as H_2O_2 diffuses through the membrane and interacts with metal ion impurities. Overall, these combined effects in mitigation of ROS concentrations account for the observed lower FRR when the $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ interlayer is positioned near the cathode, as opposed to be positioned near the anode. Polarization curves (Figure 1c) indicate a generally higher cell potential for $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (ca) than $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (an), mostly due to increased high-frequency resistance (HFR). The iR-free cell potentials for both configurations are similar, as expected. At $2\ \text{A}/\text{cm}^2$, the measured HFR for $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (ca) is $87\ \text{m}\Omega \cdot \text{cm}^2$, whereas for $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (an), it is $114\ \text{m}\Omega \cdot \text{cm}^2$ (Figure 1d). It is worth noting that the HFR varies significantly with current density in the case of $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (ca), starting to increase at $0.25\ \text{A}/\text{cm}^2$ from $84\ \text{m}\Omega \cdot \text{cm}^2$ to $114\ \text{m}\Omega \cdot \text{cm}^2$ at $3\ \text{A}/\text{cm}^2$. This may be attributed to interfacial effects resulting from an additional resistance at the interface of the membrane layers. However, the absence of such an effect for $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (an) is interesting.

[0023] Further investigation using composite membranes containing only an ionomer layer, without any $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ interlayers, confirms that the interfacial effects on HFR is only observed when the ionomer layer, and consequently the interface, is located near the cathode, instead of the anode. This may be related to an inhomogeneous distribution of mechanical stress across the membrane, as the anode is supported by a rigid Ti-felt whereas the cathode is supported by a relatively soft carbon paper, making a delamination more likely to occur near the cathode side. The differential pressure setting of 11 bar at the cathode and ambient at the anode could further exacerbate this situation. As the current density increases, the rate of electro-osmotic water drag increases proportionally, potentially causing water to accumulate inside the delaminated interface and thereby increasing the ohmic resistance. It is believed that this water can be re-absorbed into the membrane as conditions change, since the increased HFR was found to be reversible. At current densities below $0.25\ \text{A}/\text{cm}^2$, the HFRs for $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (an) and $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (ca) are comparable, falling within the CCM-to-CCM variations.

[0024] The measured H_2 in $\text{O}_2\%$ is the highest for membranes without a $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ interlayer, reaching 7.0% at $0.5\ \text{A}/\text{cm}^2$ (Figure 2b). This value decreases to 6.3% for $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (ca), and is the lowest for $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (an), at 5.4%. The incorporation of the $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ interlayer may contribute to this reduction via the following effects: I) The addition of the interlayer slightly increases the composite membrane thickness, extending the hydrogen diffusion length and therefore marginally reducing the rate of hydrogen crossover. II) The interlayer contains 50 wt% $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ particles and 50 wt% ionomer. The reduced ionomer content within the interlayer limits the available water channels for the dissolved hydrogen to diffuse through, thereby decreasing the hydrogen crossover. III) $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ particles may exhibit weak catalytic activity for the recombination of crossover hydrogen and oxygen under the current conditions, providing adsorption surfaces that facilitate the reaction.^{42,43} Given that the reactant ratio near the anode is closer to the ideal reaction stoichiometry of 2:1 for hydrogen and oxygen (as will be elaborated in a later section), this leads to a lower H_2 in $\text{O}_2\%$ for $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (an) than $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (ca). On the other hand, considering the experimental error bars in Figure 2b, the differences are only slightly more than the sample variations.

[0025] Ex-Situ Study for an Optimized Ce Content in $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ While the effectiveness of $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ with respect to its positioning has been demonstrated in the previous section, it is beneficial to further explore the optimal Ce content for radical scavenging in cerium-zirconium oxide, beyond a Ce/Zr ratio of 1. To address this question, powders of $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ with three different Ce contents ($x = 0.25, 0.5$ and 0.75) were synthesized. Phase characterization using powder X-ray diffraction (Figure 3a) reveals a peak shift towards lower 2θ angles with increasing Ce content, consistent with increased lattice spacing due to the substitution of Zr^{4+} ($0.84\ \text{\AA}$) by Ce^{4+} ($0.97\ \text{\AA}$). A gradual peak broadening is observed as the Ce content increases, which may be attributed to reduced crystallite size and/or increased lattice strain. Nitrogen physisorption measurements of the powders exhibit a type IV isotherm with a H1 type hysteresis for $\text{Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$ and $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$, and a type II isotherm with a H4 type hysteresis for $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (Figure 3b). The hysteresis feature for $\text{Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$ and $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ indicates the presence of uniformly distributed spherical or cylindrical mesopores wider than $\sim 4\ \text{nm}$. This aligns with the pore size distribution results, which show both micropores (centering at $\sim 1\text{-}2\ \text{nm}$) and mesopores (centering at $\sim 3\text{-}3.5\ \text{nm}$) for the two samples. The cumulative pore volumes are $0.146\ \text{cm}^3/\text{g}$ and $0.121\ \text{cm}^3/\text{g}$ for $\text{Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$ and $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$, respectively. Mesopores are generally absent in $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$, whose cumulative

pore volume is significantly lower, being 0.022 cm³/g. Its isotherm, with a slight hysteresis feature, indicates the presence of narrow slit-like pores. Among the three compositions, Ce_{0.25}Zr_{0.75}O₂ shows the highest BET surface area of 71 m²/g. The estimated crystallite sizes for all samples, based on the BET surface areas and by assuming spherical particles, ranges from 13 to 15 nm.

[0026] Figure 3 shows PXRD patterns of the synthesized Ce_xZr_{1-x}O₂ (x = 0.25, 0.5 and 0.75) (a), N₂ physisorption isotherms and surface areas calculated using the BET method (b), schematic illustration of the ex-situ Fenton test setup⁴⁸ (c), and fluoride concentrations monitored during the ex-situ Fenton tests (d) for these synthesized cerium-zirconium oxides.

[0027] To compare the radical scavenging performance of Ce_xZr_{1-x}O₂ with varying Ce contents, an ex-situ Fenton test was carried out. In this setup, each sample powder and a piece of Nafion NR 212 membrane were placed in a vial containing freshly prepared Fenton's reagent, as illustrated in Figure 3c. The amount of Ce_xZr_{1-x}O₂ was normalized to the same Ce mass across different compositions to ensure consistency. Fenton's reagent contains a high concentration of free radicals, which can either be scavenged by Ce_xZr_{1-x}O₂, or attack the Nafion membrane resulting in the release of fluoride. Consequently, fluoride concentration in the vial was monitored to assess the extent of the membrane degradation and, in turn, evaluate the radical scavenging activity of Ce_xZr_{1-x}O₂. As shown in Figure 3d, the suspension with Ce_{0.25}Zr_{0.75}O₂ yields the lowest fluoride concentration over the 70-hour test period, indicating its most effective radical scavenging activity under the specified conditions. Higher Ce contents (x = 0.5 and 0.75) sequentially increase the resulting fluoride concentrations, with Ce_{0.75}Zr_{0.25}O₂ demonstrating the lowest radical scavenging activity. Therefore, in the samples studied, the Ce³⁺/total Ce ratio is expected to increase in the order of: Ce_{0.75}Zr_{0.25}O₂ < Ce_{0.5}Zr_{0.5}O₂ < Ce_{0.25}Zr_{0.75}O₂. With a higher Ce³⁺ concentration, as in Ce_{0.25}Zr_{0.75}O₂, more HO[•] can be effectively scavenged via equation (1), while Ce³⁺ itself is regenerated via equation (3), leading to the observed higher radical scavenging activity. The results of X-ray photoelectron spectroscopy measurements acquired at Ce 3d core level confirmed that Ce_{0.25}Zr_{0.75}O₂ exhibited a higher Ce³⁺ concentration compared to Ce_{0.5}Zr_{0.5}O₂. However, a similarly high Ce³⁺ concentration was also observed in Ce_{0.75}Zr_{0.25}O₂, the cause of which remains unclear at this stage.

[0028] Effective Positioning of Pt Gas Recombination Interlayer and Substitution of Pt with Bi-Functional Catalyst Pt/Ce_{0.25}Zr_{0.75}O₂ Based on the findings from the previous two sections, Ce_{0.25}Zr_{0.75}O₂ was positioned as an interlayer near the cathode of the composite membrane. This configuration was maintained in subsequent experiments.

[0029] Meanwhile, the high rate of hydrogen crossover, exemplified by the blank membranes in Figure 2b, presents a significant challenge to the safe operation of the electrolysis cell. It is understood that hydrogen crossover occurs mainly through the diffusion of dissolved hydrogen gas in the aqueous domain of the hydrated membrane. The rate of hydrogen crossover typically increases with increasing cathode pressure and/or decreasing membrane thickness. While elevated cathode pressure is preferred for eliminating or reducing the need of mechanical hydrogen compression, and thin membranes are favored for reducing ohmic losses during cell operation, one approach to mitigate pronounced hydrogen crossover is to incorporate a gas recombination catalyst, such as Pt. This catalyst recombines the crossover hydrogen and oxygen to water, as:



where the ideal reaction stoichiometry for hydrogen and oxygen is 2:1. If the amounts of reactants do not meet the stoichiometric ratio, the reaction will remain incomplete. In cases where oxygen is the limiting reactant, excess hydrogen gas will continue crossing over through the membrane to the anode side, thereby leading to a high hydrogen content in the anode oxygen stream.

[0030] The ideal position inside the membrane for a gas recombination interlayer, where the crossover hydrogen and oxygen satisfy the stoichiometric ratio, is:

$$x = \left(\frac{2K_{\text{P},\text{O}_2}^{\text{diff}} p_{\text{O}_2}^{\text{an}}}{K_{\text{P},\text{H}_2}^{\text{diff}} p_{\text{H}_2}^{\text{ca}}} + 1 \right)^{-1} \cdot \delta_{\text{mem}} \quad (7)$$

[0031] Here, $K_{\text{P},\text{O}_2}^{\text{diff}}$ and $K_{\text{P},\text{H}_2}^{\text{diff}}$ are the permeability coefficients of O₂ and H₂ in the membrane, while $p_{\text{O}_2}^{\text{an}}$ and $p_{\text{H}_2}^{\text{ca}}$ are the partial pressures of O₂ and H₂, respectively. δ_{mem} is the membrane thickness. x represents the position of the gas recombination interlayer inside the membrane, with its direction pointing from the cathode towards the anode. Under the current testing conditions of 90 °C, 11 bar cathode pressure and ambient anode pressure, an interlayer position close to the anode side, where $x = 0.98 \cdot \delta_{\text{mem}}$, is determined based on extrapolation of available data.

[0032] Figure 4 shows a schematic representation of composite membrane configurations Ce_{0.25}Zr_{0.75}O₂ (ca) - Pt (ca), Ce_{0.25}Zr_{0.75}O₂ (ca) - Pt (an) and Ce_{0.25}Zr_{0.75}O₂ (ca) - Pt/Ce_{0.25}Zr_{0.75}O₂ (an) (a), fluoride release rates determined during

100-hour constant current tests (b), measured H_2 in $O_2\%$ in the current density range of 0.5-3 A/cm² (c), polarization curves and iR-free potentials (d) and the corresponding high-frequency resistances (e) for these composite membrane configurations.

[0033] To validate the effective positioning of the gas recombination interlayer, a Pt interlayer with a loading of 0.04 mg_{Pt}/cm² was incorporated near either the cathode or the anode of the composite membrane, as illustrated in Figure 4a. An ionomer layer was placed over the Pt interlayer when positioned near the anode to insulate it from the catalyst layer. In the case of the Pt interlayer positioned near the cathode, this layer was directly added onto the membrane for consistency. The anode H_2 in $O_2\%$ was measured in a range of current densities from 0.5-3 A/cm², followed by a 100-hour constant current measurement at 2 A/cm² with periodic monitoring of fluoride release rate (Figure 4b). As shown in Figure 4c, the configuration $Ce_{0.25}Zr_{0.75}O_2$ (ca) - Pt (an) indeed exhibits a generally lower H_2 in $O_2\%$ compared to $Ce_{0.25}Zr_{0.75}O_2$ (ca) - Pt (ca). At 0.5 A/cm², a reduction from 5.0% to 2.9% is seen when the Pt interlayer is changed from near the cathode to near the anode side. This observation confirms the influence of the gas recombination interlayer position, considering the yield of the recombination reaction.

[0034] On the other hand, a higher fluoride release rate was determined for $Ce_{0.25}Zr_{0.75}O_2$ (ca) - Pt (an) than for $Ce_{0.25}Zr_{0.75}O_2$ (ca) - Pt (ca) (Figure 4b), indicating an increased rate of membrane degradation when the Pt interlayer is placed near the anode. Since Pt is known to catalyze not only the gas recombination of hydrogen and oxygen, but also radical formation, a higher radical concentration is likely to induce more rapid membrane degradation when these radicals are generated far from the radical scavenger and cannot be timely scavenged, as in the case of $Ce_{0.25}Zr_{0.75}O_2$ (ca) - Pt (an). In contrast, for $Ce_{0.25}Zr_{0.75}O_2$ (ca) - Pt (ca), since the radical scavenger is positioned close to the Pt, the produced radicals can be scavenged effectively by $Ce_{0.25}Zr_{0.75}O_2$, resulting in a lower membrane degradation rate.

[0035] Figure 5 shows HAADF-STEM images of the synthesized Pt/ $Ce_{0.25}Zr_{0.75}O_2$ (a,b), with the EDX spectrum (c) acquired from the selected area in the image (Cu signals originate from the Cu grid used). The PXRD pattern with Rietveld refinement is presented in (d).

[0036] The dilemma in the use of Pt with reduced hydrogen crossover but promoted radical formation can be addressed by employing a bi-functional catalyst Pt/ $Ce_xZr_{1-x}O_2$. The substitution of Pt with Pt/ $Ce_xZr_{1-x}O_2$ concurrently mitigates hydrogen crossover and ionomer degradation. Specifically, Pt/ $Ce_{0.25}Zr_{0.75}O_2$ was synthesized via a one-pot polyol method, with calcination carried out in a reducing atmosphere. Nano-sized Pt metal particles can be directly formed on the $Ce_{0.25}Zr_{0.75}O_2$ support during the reduction of the Pt(IV)-rich layer in the calcination process of the as-prepared material. High-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images of the synthesized catalyst are shown in Figures 5a, b. Pt particles, exhibiting a relatively uniform size distribution, are clearly identified as brighter regions in the contrast, due to the higher atomic number of the element. In addition, the spectrum (Figure 5c) obtained from the selected area (Figure 5b) using energy dispersive X-ray spectroscopy (EDX) reveals Pt peaks, including the Pt L α peak at ~9.4 keV. The powder X-ray diffraction pattern of the catalyst, along with Rietveld refinement results, indicates a tetragonal-phase $Ce_{0.25}Zr_{0.75}O_2$ with a quantified Pt phase content of 4.1 wt%. This is consistent with the nominal Pt loading of 5 wt% to $Ce_{0.25}Zr_{0.75}O_2$ during synthesis (equivalent to a Pt loading of 4.8 wt% in the catalyst).

[0037] Substitution of Pt with a Pt/ $Ce_{0.25}Zr_{0.75}O_2$ interlayer near the anode in the composite membrane leads to the configuration $Ce_{0.25}Zr_{0.75}O_2$ (ca) - Pt/ $Ce_{0.25}Zr_{0.75}O_2$ (an), as illustrated in Figure 4a. This configuration exhibits the lowest fluoride release rate, measured at 0.023 ($\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$) at the end of the 100-hour constant current test (Figure 4b). Its average FRR of 0.028 ± 0.008 ($\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$) represents a 3.6-fold reduction compared to $Ce_{0.25}Zr_{0.75}O_2$ (ca) - Pt (ca) (0.10 ± 0.01 ($\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$)). In the meantime, it also demonstrates the lowest H_2 in $O_2\%$ (Figure 4c), recorded at 1.6% at 0.5 A/cm², corresponding to a 45% decrease relative to $Ce_{0.25}Zr_{0.75}O_2$ (ca) - Pt (an). Given the same Pt loading, this decrease in the recorded H_2 in $O_2\%$ may be attributed to the highly dispersed Pt nanoparticles on the $Ce_{0.25}Zr_{0.75}O_2$ support in the Pt/ $Ce_{0.25}Zr_{0.75}O_2$ interlayer, providing more active surface area for efficient gas recombination, whereas they tend to remain agglomerated in the spray-coated Pt interlayer in $Ce_{0.25}Zr_{0.75}O_2$ (ca) - Pt (ca). Notably, compared to the 7.0% H_2 in $O_2\%$ measured in the blank membranes (Figure 2b) at 0.5 A/cm², a 4.4-fold reduction is achieved when using the configuration $Ce_{0.25}Zr_{0.75}O_2$ (ca) - Pt/ $Ce_{0.25}Zr_{0.75}O_2$ (an).

[0038] The measured FRR allows to estimate the projected lifetime of the membrane. For this, it is assumed that membrane end of life is marked by a loss of 10% of its fluoride inventory. For Nafion NR 212 with a dry thickness of 50 μm , assuming a constant FRR of 0.023 ($\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$) at a cell temperature of 90°C, which was measured at the end of the 100-hour constant current test, this yields a membrane lifetime of 29,000 h. Compared to blank measurements without any functional catalyst particle interlayers, it represents a 7.4 times increase in the projected membrane lifetime. Using an activation energy for membrane degradation of 58 kJ/mol, this translates to a lifetime of 50,000 h at 80°C and 89,000 h at 70°C.

[0039] It has to be pointed out that other degradation mechanisms and failure modes were neglected here, such as catalyst aging and mechanical degradation of the membrane, for example caused by creep. Moreover, it is assumed that the activity of the ceriazirconia radical scavenger is maintained over this time period. Thus, these results showcase the effectiveness of the synthesized Pt/ $Ce_{0.25}Zr_{0.75}O_2$ embedded as an interlayer in the composite membrane, in mitigating radical-induced ionomer degradation and hydrogen crossover. Based on the outcomes of the current experimental work in

view of the present invention, the composite membrane $Ce_{0.25}Zr_{0.75}O_2$ (ca) - $Pt/Ce_{0.25}Zr_{0.75}O_2$ (an) demonstrates promising potential for application as next-generation catalyst coated membranes in PEM water electrolysis cells.

[0040] As shown in Figure 4d, the substitution with a thicker $Pt/Ce_{0.25}Zr_{0.75}O_2$ interlayer compared to Pt results in an increased cell potential in the polarization curve, mainly due to a pronounced increase in HFR (Figure 4e). This could result from both an increased membrane thickness and enhanced interfacial effects. Alternative composite membrane fabrication methods beyond spray coating should be explored to improve interfacial properties. Additionally, optimizing the loadings of $Ce_{0.25}Zr_{0.75}O_2$ and $Pt/Ce_{0.25}Zr_{0.75}O_2$, as well as the interlayer ionomer-to-catalyst ratio could help achieve an optimal balance between membrane electrical resistance and the functional performance of the interlayer.

[0041] Figure 6 schematically shows again the principle of an electrochemical cell comprising a composite proton exchange membranes with interlayer structures having a high capability of an effective radical scavenger and of reducing the hydrogen cross-over when using thin membranes.

Claims

1. Electrochemical cell comprising a catalyst coated membrane, i.e. for use in water electrolysis, wherein:
 - i) the membrane is a cation exchange membrane (CEM), in particular a proton exchange membrane (PEM) or an anion exchange membrane (AEM), in particular a hydroxide exchange membrane (HEM);
 - ii) said membrane having a thickness below 100 μm , preferably below 75 μm , more preferably below 50 μm ; and
 - iii) said membrane comprises an antioxidant (AO) and a gas recombination catalyst (GRC) in the form of micro and/or nanoparticles, preferably in form of a layer of antioxidant particles and a layer of gas recombination catalyst particles that are placed within the membrane close to the cathode side and the anode side, respectively.
2. Electrochemical cell according to claim 1, wherein the antioxidant is an oxide of the type $Ce_{1-x-y}Zr_{1-x-y}M_1M_2M_3O_{2-d}$ comprising cerium as a redox-active transition metal, wherein M1 is one or more transition metals, M2 is one or more lanthanide metals, M3 is one of more noble or heavy metal, with $0 < x, y, z < 1$ and $2-d$ expresses the oxygen stoichiometry with $-0.5 < d < 0.5$.
3. Electrochemical cell according to claim 2, wherein the oxide is of the type cerium oxide (CeO_{2-d}), cerium-zirconium oxide ($Ce_xZr_{1-x}O_{2-d}$), cerium-gadolinium oxide ($Ce_xGd_{1-x}O_{2-d}$), preferably: $Ce_xZr_{1-x}O_{2-d}$ with $0.1 \leq x \leq 0.75$ and more preferably $0.2 \leq x \leq 0.5$, or the oxide is a metal organic framework (MOF) with Ce(III)/Ce(IV) as metal center, such as Ce-MOF-808.
4. Electrochemical cell according to any of the preceding claims, wherein the gas recombination catalyst is:
 - a) a noble metal black, preferably Pt or Pd or an alloy of Pt and Pd, and/or
 - b) a noble metal, as described in a), supported on the antioxidant, preferably supported on $Ce_xZr_{1-x}O_{2-d}$, such as Pt supported on $Ce_xZr_{1-x}O_{2-d}$ (Pt- $Ce_xZr_{1-x}O_{2-d}$) with a Pt content with respect to the oxide of preferably 1 to 20 wt-% and more preferably 2 to 10 wt-%, and/or
 - c) a noble metal, as described in a), inserted into the cavity of a MOF type antioxidant.
5. Electrochemical cell according to any of the preceding claims, wherein said membrane is a proton exchange membrane of the perfluoroalkylsulfonic acid (PFSA) type, for example Nafion[™] (Chemours), Fumapem[®] and Fumasep[®] (Fumatech) or Aquivion[®] (Syensqo) or a proton exchange membrane of the hydrocarbon type, for example Pemion[™] (Ionomr) or an AEM, for example PiperION[®] (Versogen), Aemion[™] (Ionomr), Aemion+[™] (Ionomr), Duraion[®] (Creavis), Durion[™] (Xergy), Fumasep[®] (Fumatech), Sustainion[®] (Dioxide Materials).
6. Electrochemical cell according to any of the preceding claims, wherein the antioxidant particles are mixed with the same type of ionomer, optionally with a different equivalent weight, in dispersed form, that the membrane is made of and the resulting slurry is deposited onto the cathode side of the membrane by one or more of:
 - a) coating
 - b) printing
 - c) spraying

d) decal transfer,

wherein an antioxidant (AO) loading ranges from 0.01 to 2 mgAO/cm², more preferably 0.05 to 0.2 mgAO/cm², with a layer thickness of <10 μm, and wherein a further layer of the pure ionomer is added by one of the afore-mentioned methods with a thickness of less than 10 μm;

or

the antioxidant particles are incorporated into a cathode catalyst layer comprising an electrocatalyst for the hydrogen evolution reaction (HER), for example Pt/carbon, with a preferable load of the antioxidant (AO) in the range from 0.01 to 2 mgAO/cm², more preferably 0.05 to 0.2 mgAO/cm², and wherein the HER catalyst is a Pt/carbon catalyst, and the Pt loading of the cathode catalyst layer is preferably between 0.010 and 0.40 mgPt/cm², more preferably between 0.025 and 0.10 mgPt/cm².

7. Electrochemical cell according to any of the preceding claims, wherein

the gas recombination catalyst particles are mixed with the same type of ionomer, in dispersed form, that the membrane is made of, and the resulting slurry is deposited onto the anode side of the membrane, by one or more of

- a) coating;
- b) printing;
- c) spraying;
- d) decal transfer;

wherein a load of the gas recombination catalyst in terms of its noble metal content ranges from 0.001 to 0.1 mg(noble metal)/cm², more preferably 0.02 to 0.05 mg(noble metal)/cm², with a layer thickness below 10 μm and wherein a further layer of the pure ionomer is added by one of afore-mentioned methods with a thickness of less than 10 μm.

8. Electrochemical cell according to any of the preceding claims, wherein

the catalyst coated membrane (CCM) is prepared by coating an anode and cathode catalyst layer onto the composite membrane comprising a layer of the gas recombination catalyst particles near the anode side of the membrane and a layer of the antioxidant particles near the cathode side of the membrane, unless the antioxidant particles are incorporated into the cathode catalyst layer.

9. Electrochemical cell according to any of the preceding claims, wherein

the composition of the anode catalyst layer comprises a catalyst for the oxygen evolution reaction (OER), such as IrO_x, IrO_x supported on TiO₂, IrO_x supported on another oxide; or IrRuO_x, IrRuO_x supported on oxide; or, in the case of AEMWE, any oxide containing transition metals, such as NiFe layered double hydroxide (LDH)-based electrocatalyst, and an ionomer, which optionally is of the same type as the ionomer constituting the membrane, or of a different class of ionomer.

10. Electrochemical cell according to any of the preceding claims, wherein

the composition of the cathode catalyst layer comprises a catalyst for the hydrogen evolution reaction (HER), such as Pt black or Pt supported on carbon (Pt/C), or Pd black or Pd supported on carbon (Pd/C), or an alloy black containing Pt or Pd or both, or a carbon supported catalyst containing Pt or Pd or both, and an ionomer, which optionally is of the same type as the ionomer constituting the membrane, or of a different class of ionomer.

11. Electrochemical cell according to any of the preceding claims, wherein

for the deposition process, an ink is formed from the respective catalyst and the respective ionomer using a solvent to obtain a slurry or paste, wherein the solvent is an organic solvent, water, or a mixture thereof.

12. Electrochemical cell according to any of the preceding claims, wherein

the anode and the cathode catalyst layer are deposited by one of more of:

- a) coating
- b) printing
- c) spraying
- d) decal transfer.

13. Electrochemical cell according to any of the preceding claims, wherein the catalyst coated membrane CCM is assembled into a water electrolyzer cell with the addition of the following components:

- i) a carbon based gas diffusion layer (GDL) on the cathode side
- ii) a titanium based porous transport layer (PTL) on the anode side
- iii) optionally a sub-gasket for edge protection; and
- iv) suitable seals and gaskets.

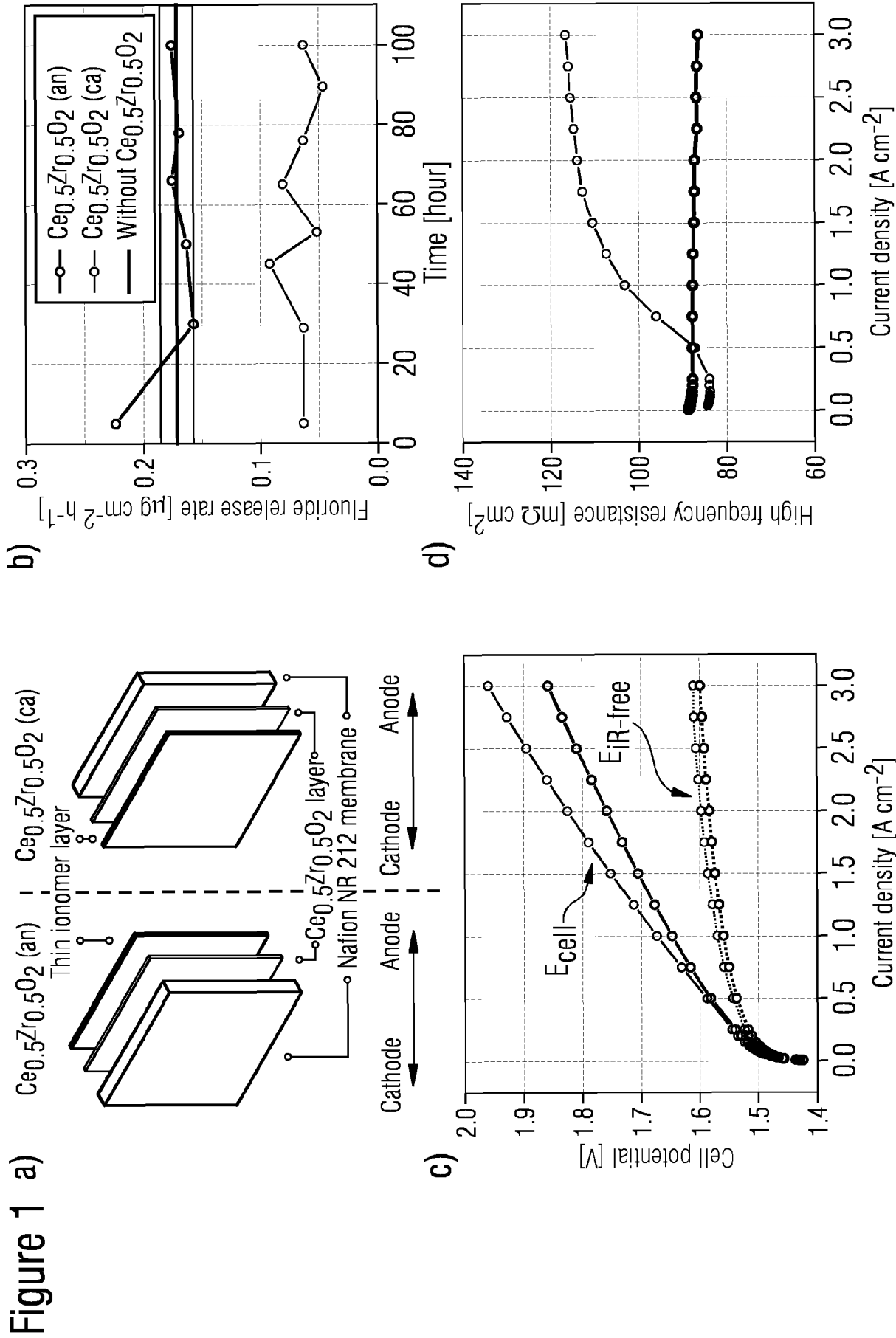
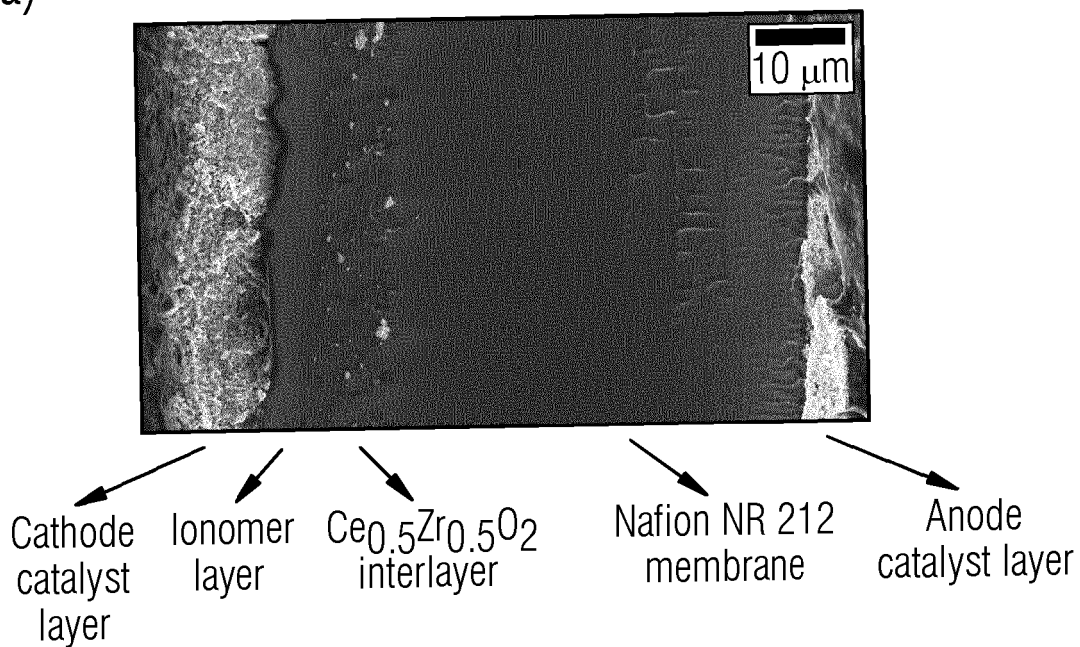


Figure 2

a)



b)

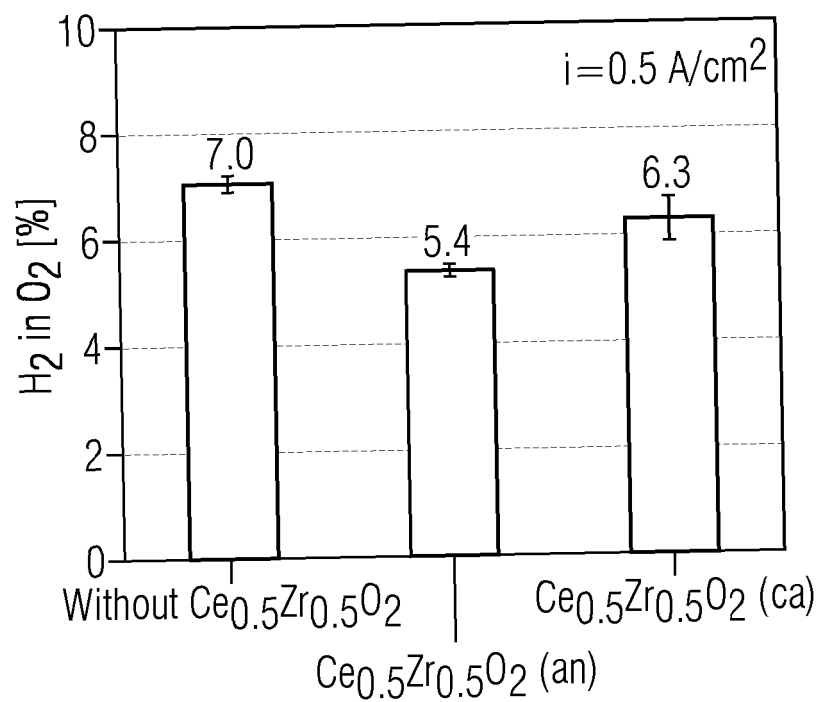


Figure 3

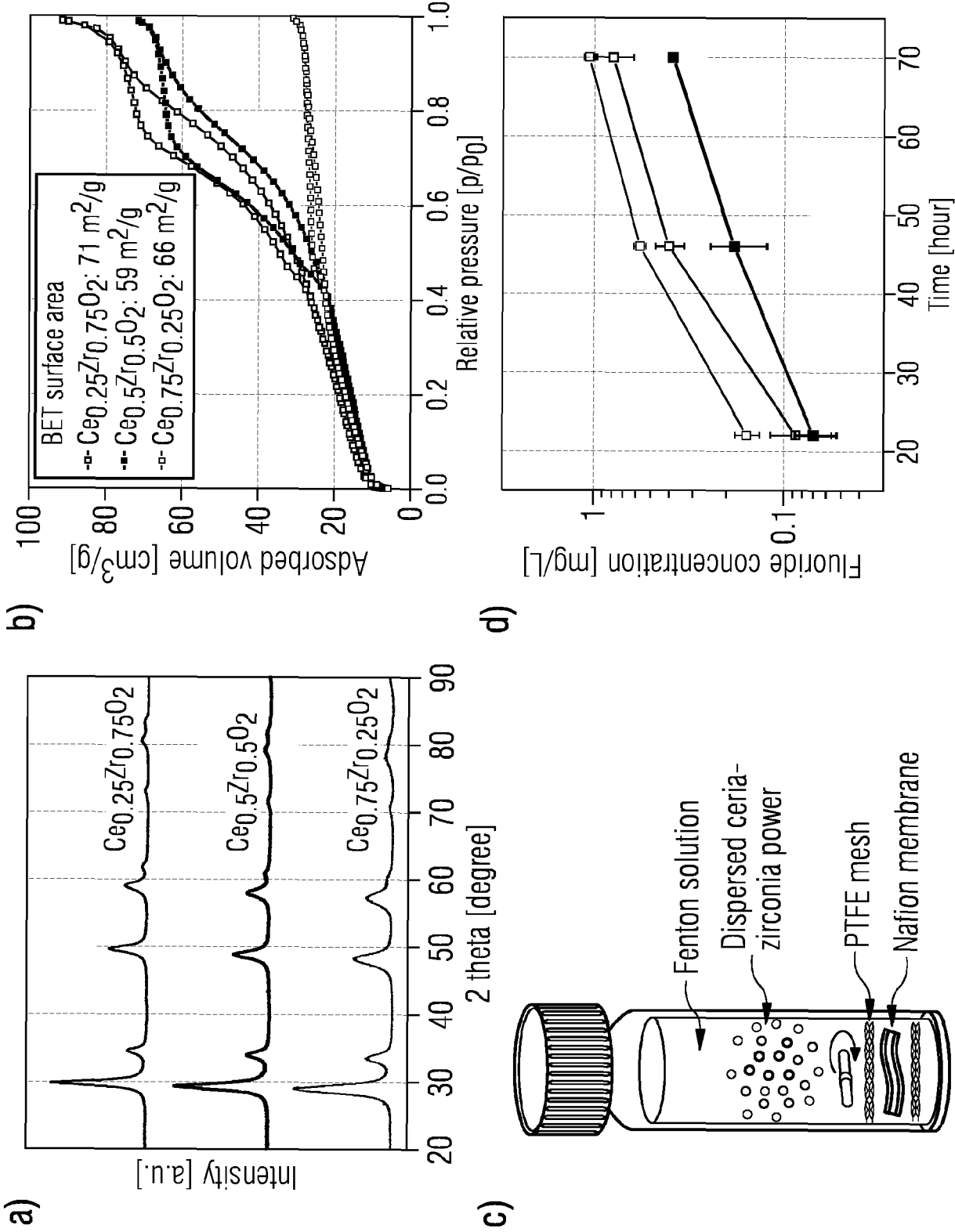
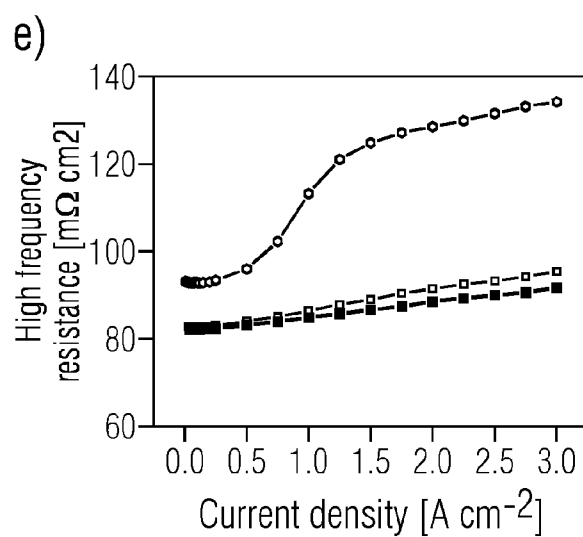
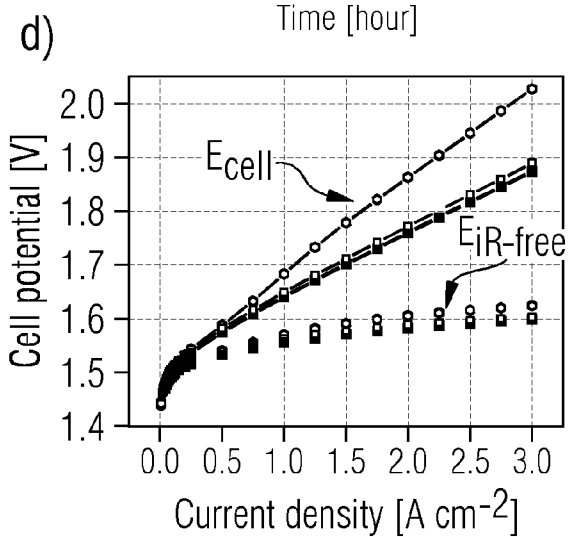
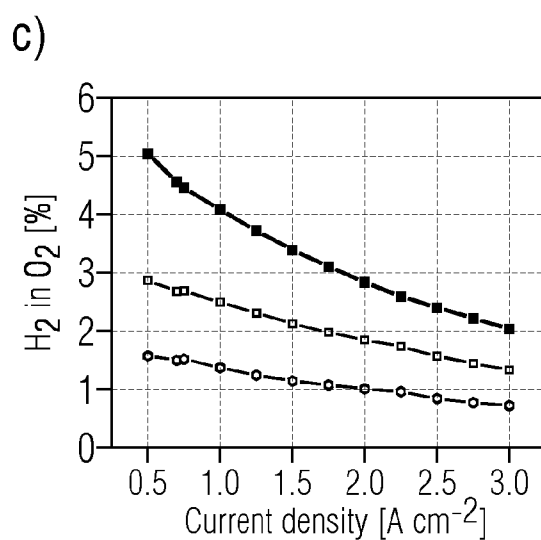
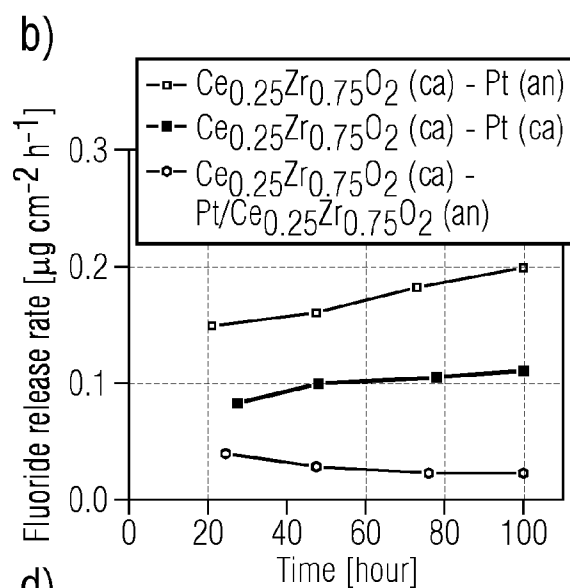
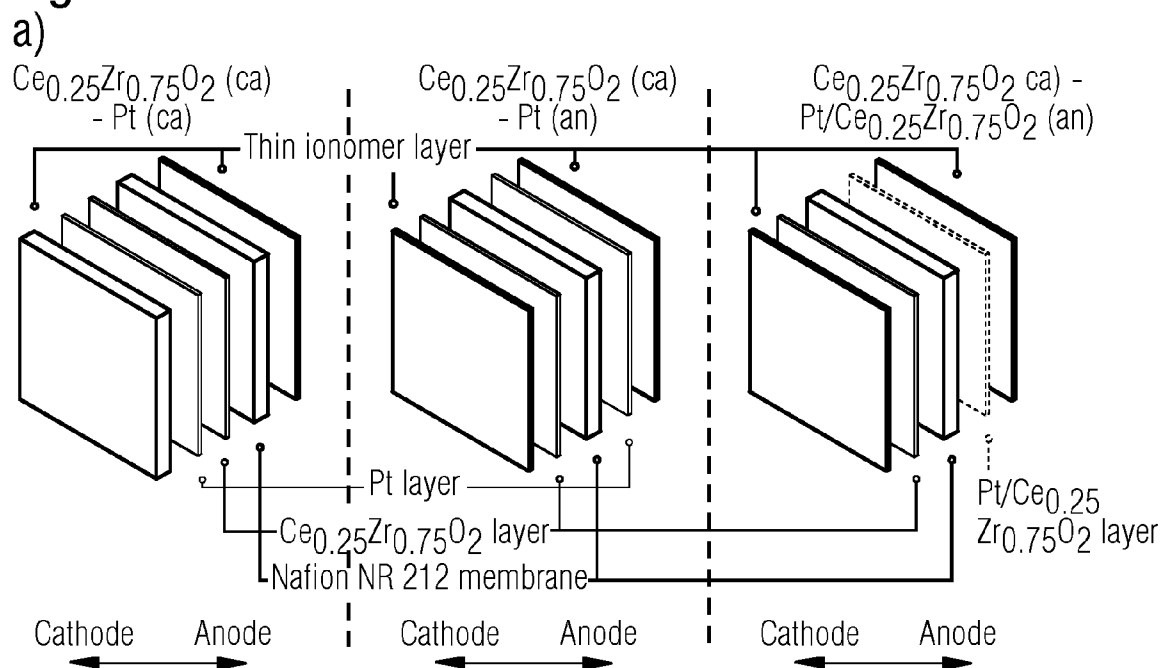


Figure 4



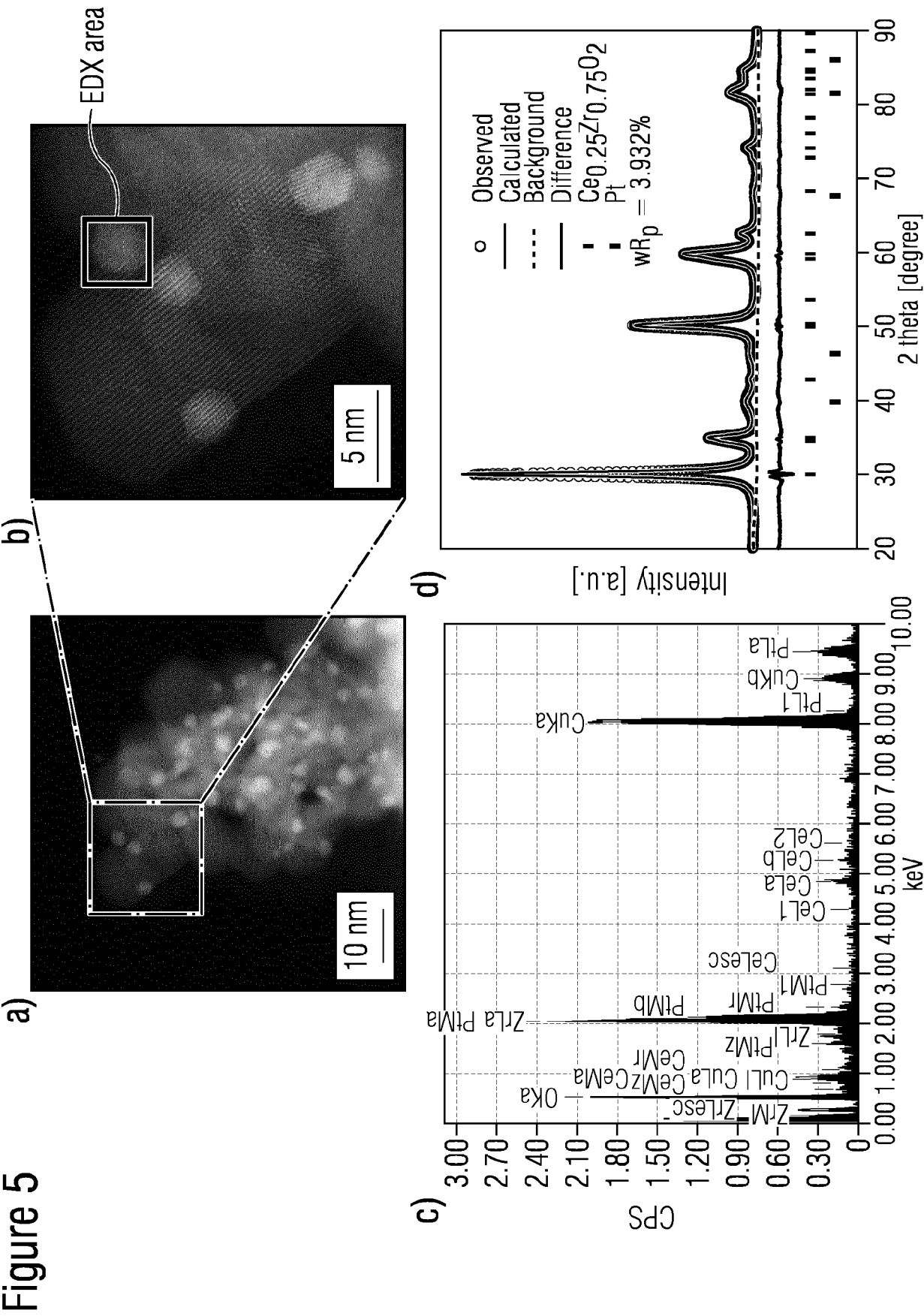
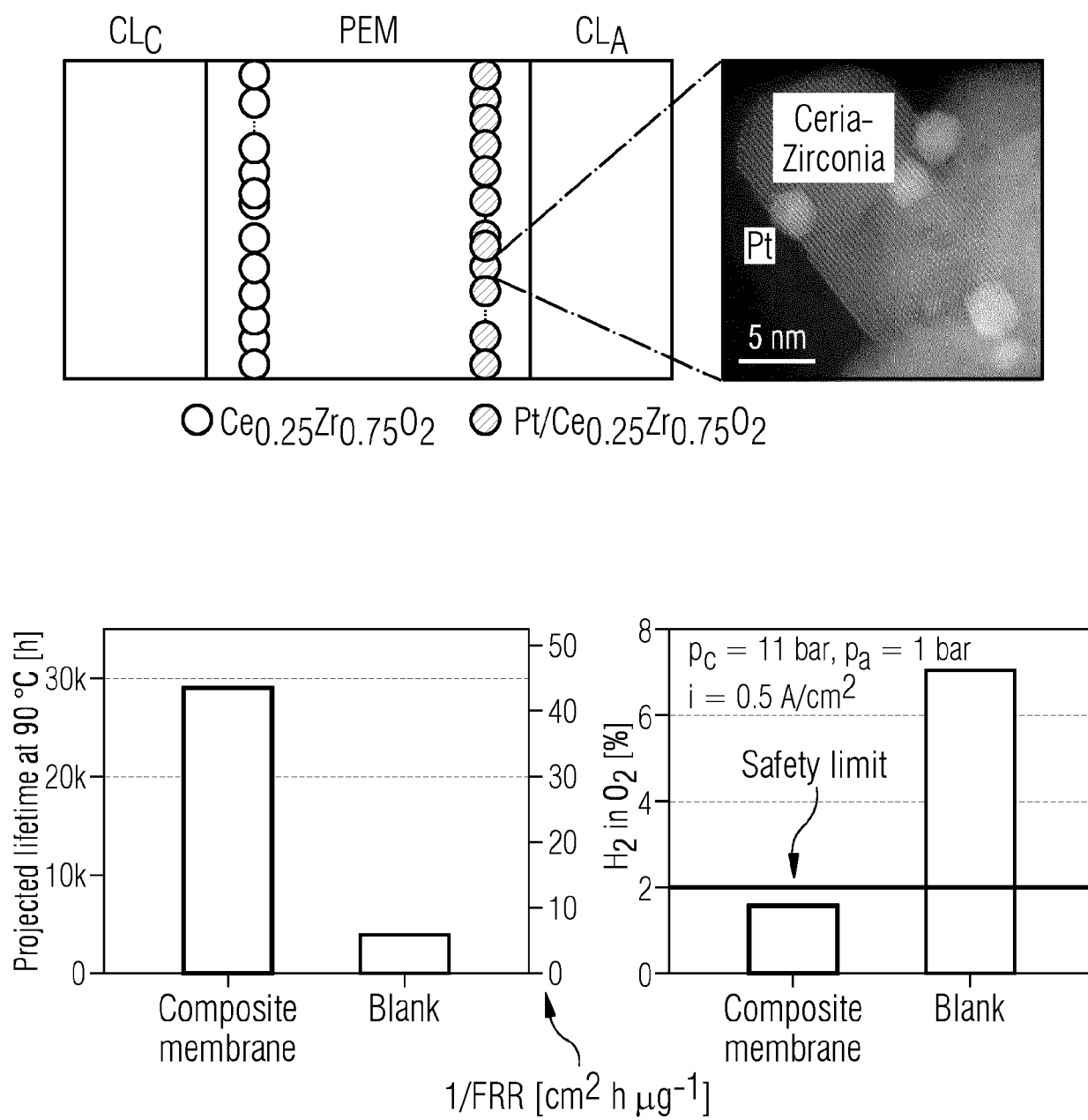


Figure 5

Figure 6





EUROPEAN SEARCH REPORT

Application Number

EP 25 16 8162

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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EUROPEAN SEARCH REPORT

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