



The chemical behavior and degradation mitigation effect of cerium oxide nanoparticles in perfluorosulfonic acid polymer electrolyte membranes



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ABSTRACT

Perfluorosulfonic acid membranes are susceptible to degradation during hydrogen fuel cell operation due to radical attack on the polymer chains. Mitigation of this attack by cerium-based radical scavengers is an approach that has shown promise. In this work, two formulations of crystalline cerium oxide nanoparticles, with an order of magnitude difference in particle size, are incorporated into said membranes and subjected to proton conductivity measurements and ex-situ durability tests. We found that ceria is reduced to Ce(III) ions in the acidic environment of a heated, humidified membrane which negatively impacts proton conductivity. In liquid and gas Fenton testing, fluoride emission is reduced by an order of magnitude, drastically increasing membrane longevity. Sideproduct analysis demonstrated that in the liquid Fenton test, the main point of attack is weak polymer end groups, while in the gas Fenton test, there is additional side-chain attack. Both mechanisms are mitigated by the addition of the ceria nanoparticles, whereby the extent of the concentration-dependent durability improvement is found to be independent of particle size.

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1. Introduction

Perfluorosulfonic acid (PFSA) ionomers are the polymer class of choice for polymer electrolyte membrane (PEM) fuel cells. They combine high proton conductivity, a key parameter for achieving good performance, with high thermal and mechanical stability. Next to their high cost, which is a significant barrier to the commercialization of fuel cells, their main weakness is their relative susceptibility towards degradation under fuel cell conditions.

Due to the reactions between crossover hydrogen and oxygen in the presence of platinum, as well as other metal impurities, hydrogen fuel cell operation results in the formation of the hydroxyl radical, HO•, either from hydrogen peroxide [1,2] or directly

on the catalyst [3,4]. The HO• initiates a series of degradation mechanisms that mainly involve hydrogen abstraction from membrane carboxylic acid (COOH) or sulfonic acid groups or attack on ether-adjacent carbon atoms on the side-chain, with the formation of H₂O, CO₂ and HF along with larger polymer fragments [5,6]. The cell's performance decreases due to a loss in the membrane's proton conductivity and increased gas crossover, which itself accelerates degradation and finally results in pinhole or other defect formation and ultimately catastrophic failure of the membrane.

Numerous materials are capable of mitigating the effect of radicals and many have been tested in hydrogen fuel cells, such as platinum, palladium, gold, silver, titania, silica, cerium oxide and manganese oxide nanoparticles, as well as heteropolyacids and cations, such as Ce³⁺ and Mn²⁺ [7–13].

Of these, the Ce³⁺/Ce⁴⁺ redox couple has received the most research attention due to its notable ability to facilitate switch back and forth between its two oxidation states. Consequently, PFSA membranes have been ion-exchanged with low levels of cerium

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ions and open circuit voltage (OCV) hold tests have shown a decrease in the fluoride emission (FE) rate, a good measure of membrane degradation, by up to three orders of magnitude over a period of 200 h [11]. However, the exchange of some of the proton sites by Ce^{3+} ions leads to a reduction in proton conductivity and performance. Furthermore, there have been indications that the ions leach from the membrane, making them inadequate for long-term use. As an alternative approach to Ce^{3+} ion exchange, addition of cerium in the form of cerium oxide (ceria) has been explored [9,14]. The premise of this approach has been based on the fact that cerium, as part of the lattice structure, retains its ability to act as a redox couple [15–18] without causing a reduction in the membrane's proton conductivity due to ionic exchanges with the sulfonic acid sites [9,14]. In a previous publication, our group showed the exceptional degradation mitigation ability of cerium oxide nanoparticles in 500 h OCV hold tests [19,20]. Following Department of Energy described accelerated test protocols, the additive was found to decrease fluoride emission by at least two orders of magnitude with low, recoverable OCV decay and no impact on performance, resulting in a nearly pristine membrane after 500 h of extreme chemical degradation conditions.

This paper extends that work by focusing on the characterization of the cerium oxide formulations and its chemical behavior in PFSA membranes. Further, its degradation mitigation effects in *ex-situ* accelerated membrane durability tests are presented.

2. Experimental

2.1. Materials preparation

Cerium oxide was synthesized by a thermal hydrolysis method which, after cleaning and drying, was dispersed in ethanol. A commercially available material (Alfa Aesar, 99.9% min (REO)) was also used. Both were incorporated, at three concentration levels (0.5, 1.0 and 2.0 wt% of cerium oxide relative to the polymer mass), into polytetrafluoroethylene (PTFE)-supported PFSA membranes by casting from a dispersion of PFSA in alcohols and dimethylformamide as described in an earlier work [19]. Membranes without ceria were also cast as baselines.

2.2. Electron microscopy

An aberration-corrected JEOL 2200FS TEM/STEM instrument equipped with a Bruker Quantax EDS detector was used to perform scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDS) on ceria powders. Scanning electron microscopy (SEM) imaging of membrane cross-sections was performed on a Hitachi TM3000 SEM with an integrated Physical Electronics 5400 EDS sensor.

2.3. UV/Vis and NMR spectroscopy

Transmission UV/Vis spectra were obtained on a Shimadzu UV-2401PC. ^{19}F NMR measurements were performed on a Varian VNMRS 500 MHz instrument.

2.4. Proton conductivity

The resistance of membranes was measured using a Princeton Applied Research Potentiostat/Galvanostat Model 263A by performing cyclic voltammetry from -0.3 to 0.3 V at a rate of 30 mV s^{-1} on a piece of membrane in a 4-probe BakkTech conductivity cell under a $1000\text{ cm}^3\text{ min}^{-1}$ hydrogen gas flow (Airgas, Inc.; UHP) at $80\text{ }^\circ\text{C}$. The relative humidity of the gas stream was

varied from 20 to 90% and the in-plane conductivity of the membranes was calculated based on the membrane dimensions.

2.5. Fenton testing

For Fenton tests, membranes were ion-exchanged with Fe^{2+} ions by immersing in a 200 ml solution of FeSO_4 (Acros Organics; 99.5% for analysis) in a mole ratio of 10:1 of protons to Fe^{2+} .

For liquid Fenton tests (LF), Fe^{2+} ion-exchanged membranes were immersed in 3.0% hydrogen peroxide solutions (VWR; diluted from 30%; ACS Grade) under reflux conditions at $80\text{ }^\circ\text{C}$ for 48 h. After 24 h, using test strips (EMD Chemicals; $100\text{--}1000\text{ mg dm}^{-3}$ H_2O_2), the hydrogen peroxide was found to be completely decomposed and hence the solution was replaced to replenish the hydrogen peroxide content.

The gaseous Fenton test (GF) was modeled on a setup devised by Hommura et al. [21] and Endoh et al. [22]. Fe^{2+} ion-exchanged membranes, in an $80\text{ }^\circ\text{C}$ reaction chamber, were exposed to a $50\text{ cm}^3\text{ min}^{-1}$ flow of nitrogen gas (Airgas, Inc.; UHP) that was previously bubbled through a $60\text{ }^\circ\text{C}$ solution of 30% hydrogen peroxide. Off-gases were passed through a potassium hydroxide solution (VWR; 0.1 M; Baker Analyzed) that trapped any degradation products. Fluoride concentrations for the Fenton tests were measured by ion chromatography on a Dionex ICS-1500 equipped with AS9-HC carbonate eluent anion-exchange column.

3. Results and discussion

3.1. Membrane proton conductivity

One important metric of an ionomer's suitability as a membrane for PEM fuel cells is its ability to conduct protons. PFSA ionomers used in fuel cells are able to transport protons by either diffusion through absorbed water or by the Grotthuss mechanism [23]. If additives inhibit either of these two mechanisms, their incorporation into PFSA membranes can have a detrimental effect on proton conduction and therefore performance [5,12,13,24].

The experimental method for proton conductivity measurements involved holding membranes at various relative humidity levels and allowing enough time for the membrane to reach a steady-state condition. However, for ceria-containing membranes, the conductivity was found to slowly but continually decrease over time, with a concurrent decrease in membrane opacity. To determine the cause of this phenomenon, the proton conductivity was measured while holding the membranes at $80\text{ }^\circ\text{C}$ and 70% RH for up to four days, as plotted in Fig. 1.

Over 30 h of measurement, no significant change in the conductivity of the baseline material is observed, yielding a typical value of 35 mS cm^{-1} for PFSA membranes [9]. Both ceria-containing membranes, on the other hand, show a greater than three-fold decrease in proton conductivity and did not reach a minimum even after 18 and 90 h of testing for the synthesized and commercial ceria, respectively (the increase in conductivity for the synthesized material at ~ 18 h is discussed further below).

In order to gain a better understanding of the loss in membrane opacity and decrease in proton conductivity, further tests were conducted. Fig. 2a and c shows SEM images of the cross-sections of the synthesized ceria-containing membrane before and after 18 h of measurements at $80\text{ }^\circ\text{C}$ and 70% RH, respectively. Before testing, the precipitation of ceria onto the PTFE support is clearly visible as an intermittent band of white nanoparticles. These agglomerates, confirmed by EDS analysis (Fig. 2b) to contain cerium are no longer observable after conductivity testing (Fig. 2c).

However, EDS mapping of a 6 h tested membrane, shown in Fig. 2d, clearly demonstrates the presence of cerium, as seen by the

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