



## The degradation mitigation effect of cerium oxide in polymer electrolyte membranes in extended fuel cell durability tests

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### H I G H L I G H T S

- ▶ Ceria nanoparticles incorporated into polymer electrolyte fuel cell membranes.
- ▶ Ceria decreases open-circuit voltage decay and fluoride emission in 94 h tests.
- ▶ Ceria decreases platinum deposition and broadens platinum band.
- ▶ Ceria remains effective over 500 h, resulting in almost no membrane degradation.

### A R T I C L E I N F O

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### A B S T R A C T

In this work, two formulations of cerium oxide nanoparticles were incorporated into perfluorosulfonic acid membrane electrode assemblies (MEAs) and their ability to improve the in-situ membrane durability was studied by subjecting them to 94 and 500 h open-circuit voltage hold accelerated durability tests. In the shorter test the open circuit voltage decay rate was reduced by half and the fluoride emission by at least one order of magnitude, though no effect on hydrogen crossover or performance on the baseline MEAs was measured. The presence of the additive increased the particle size but decreased the number of platinum catalyst particles that were deposited in the membrane. The main Pt band was found at the predicted location; however, the incorporation of ceria caused a broadening with particles reaching further into the membrane. In 500 h tests, ceria-containing MEAs demonstrated a seven-fold decrease in open-circuit voltage decay and three orders of magnitude reduction in fluoride emission rates with unchanged performance and hydrogen crossover, remaining effectively pristine whilst the baseline MEA underwent catastrophic failure.

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### 1. Introduction

Polymer electrolyte membrane hydrogen fuel cells have the potential to become a large-scale source of clean stationary or portable electrical power, especially when combined with renewable energy production methods such as solar and wind. They are the leading technology able to provide a driving experience that is comparable, in terms of range and refueling behavior, to vehicles equipped with internal combustion engines. Currently, no membrane is able to withstand the harsh conditions of a hydrogen fuel cell

environment for the more than 5000 h in automotive applications that are required for commercialization. Mechanical stresses such as swelling due to changes in relative humidity, differential gas pressures and compression combined with chemical attack cause membranes to degrade to such an extent that the cell fails [1].

The mechanisms of perfluorosulfonic acid (PFSA) ionomer chemical degradation are still the focus of much debate, however, there is a general consensus that reactive oxygen species such as hydroxyl or hydroperoxyl radicals are the main reagents. They are thought to form either directly in a reaction between hydrogen and oxygen on platinum or from hydrogen peroxide, which is formed at the electrodes, decomposition with metal impurities in the fuel cell [2]. These radicals attack vulnerable groups of the PFSA polymer, degrading the membrane [1,3–7].

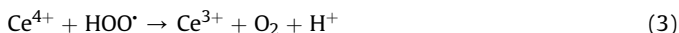
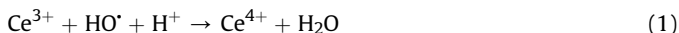
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Due to the large time scales involved in testing cells in real life conditions, accelerated durability test protocols have been developed [1]. In the open circuit voltage (OCV) hold test, cells are exposed to hydrogen and air or oxygen at low relative humidity (<50% RH) and open-circuit voltage, sometimes under pressure. At OCV conditions, insignificant amounts of the reactants are consumed and the gas crossover is maximized, leading to maximum production of radicals [8]. Consequently, the OCV hold test is often used as a method for specifically testing membrane degradation and the 500 h test protocol that is employed in this study has been established by the Department of Energy.

Several methods have been employed to reduce membrane degradation, including development of chemically stabilized membranes [9,10], mechanically reinforced membranes [11–16], alternate electrode materials [17–19] and the incorporation of hydrogen peroxide decomposition [11,12,20,21] or radical scavenging materials [6,21–33]. The latter approach is utilized in this research.

One of the most researched radical scavenging materials is the Ce(III)/Ce(IV) redox couple. This lanthanide is able to facilitate switch between its two oxidation states, allowing it to quench radicals by donation or acceptance of electrons. The quenching reaction of HO· by the Ce<sup>3+</sup> ion is given in Eq. (1). Cerium oxide also known as ceria can act catalytically by returning to its Ce(IV) oxidation state through reaction with hydrogen peroxide, as shown in Eq. (2), or the hydroperoxyl radical, as shown in Eq. (3) [25,34]. In ceria, the cerium ions retain this radical scavenging behavior while bound in their oxide lattice. The ability of ceria to scavenge radicals is well known, especially in biological and medical applications [35–39].



In fuel cells, ion-exchanged PSFA membranes with low concentrations of Ce<sup>3+</sup> ions have shown a 1000-fold reduction in fluoride emission rate (FER) over 200 h in OCV hold tests [34]. As a result of the ion-exchange, a noticeable reduction in performance and proton conductivity was measured. In order to avoid this detrimental effect, cerium oxide was added to recast membranes and was found to reduce FER by one order of magnitude without impacting performance over a 24 h test. This durability improvement was observed to be independent of nanoparticle concentration and formulation [25]. In a comparable work by Xiao et al., the OCV decay rate was found to be on the order of 0.1 mV h<sup>-1</sup> for a 150 h OCV hold test, a sixty-fold reduction compared to a baseline MEA [6].

Most of the testing reported in the literature was short in duration. As a result, the ability of ceria to act catalytically over longer periods of time (hundreds of hours in accelerated tests) needs to be established. Furthermore, as a redox-active material, ceria can affect the potential profile present due to crossover hydrogen and oxygen. Its effect on the deposition of Pt catalyst within the membrane has not been determined. This work focuses on both long term degradation studies and ceria's effect on Pt band formation.

## 2. Experimental

### 2.1. Materials preparation

Nanoparticulate ceria was prepared by thermal hydrolysis. Ammonium hydroxide, 0.50 ml, (Fisher Scientific; 29.04%) was added to 50 ml of a boiling solution of 0.02 M ammonium cerium nitrate (Acros Organics; 99.5% for analysis) in ethanol (Decon Labs;

200 proof) which, after the addition, was left to cool overnight under constant stirring. The yellow precipitate of cerium oxide that formed was centrifuged, washed five times with 5 ml of ethanol and then dried at 100 °C under vacuum, yielding ca. 0.17 g of product with particle sizes in 2–5 nm range.

The synthesized ceria was dispersed in ethanol in a Branson 2510 ultrasound bath using sonication at 40 kHz to give 7 mM colloidal dispersions in ethanol. Using the same technique, 7 mM dispersions of a commercial cerium oxide powder (Alfa Aesar; 99.9% min (REO), 20–150 nm) in ethanol were also prepared.

PFSA membranes were cast onto a porous PTFE support (Donaldson Filtration Solution; Tetratex® membrane; 7 μm) from solutions of 5% 1100 EW PFSA dispersions in alcohols (Ion Power, Inc.), ethanol and dimethylformamide (Acros Organics; 99.5% for HPLC) in a 5.8:4.0:1.0 volume ratio. Ceria was incorporated by replacing some of the ethanol with appropriate amounts of the ethanol dispersions to yield 0.5, 1.0 and 2.0 weight percent of cerium oxide relative to the polymer mass. Membranes without ceria were also cast as baselines. After room temperature drying, membranes were heated at 150 °C for 3 h under vacuum after purging three times with UHP nitrogen to remove all residual solvent.

### 2.2. Membrane electrode assembly fabrication (MEA)

A homogenized dispersion of a platinum on carbon powder (Tanaka; 46.7% Pt on C) in a methanol (Acros Organics; 99.9% for HPLC), deionized water and 5% 1100 EW PFSA in alcohol (Ion Power, Inc.) mixture was sprayed onto the membranes to give 25 cm<sup>2</sup> catalyst coated membranes (CCMs). Catalyst loadings were determined gravimetrically and kept at 0.375 ± 0.025 gPt cm<sup>-2</sup>. The CCMs were ion-exchanged with cesium ions by immersing in a 0.05 M CsCO<sub>3</sub> (Alfa Aesar; 99% (metals basis)) solution overnight, followed by a 5 min hot press at 180 °C and then reprotonated by immersion in 0.5 M H<sub>2</sub>SO<sub>4</sub> (BDH; 95.0%). The CCMs were built into 25 cm<sup>2</sup> hardware (Fuel Cell Technologies) with gas-diffusion layers (GDL) purchased from Ion Power, Inc. (Sigracet 10BC).

### 2.3. Single cell evaluation

#### 2.3.1. Initial cell integrity tests

Internal and external leak tests were performed at room temperature. The absence of cell shorts was verified using a multimeter.

**Table 1**  
List of MEAs and OCV hold conditions.

MEA	Ceria	# of cells		
<b>94 h OCV hold</b>				
Baseline	None	3		
Synthesized ceria	0.5 wt%	2		
Synthesized ceria	1.0 wt%	2		
Synthesized ceria	2.0 wt%	2		
Commercial ceria	0.5 wt%	2		
Commercial ceria	1.0 wt%	2		
Commercial ceria	2.0 wt%	2		
<b>500 h OCV hold</b>				
Baseline	None	1		
Synthesized ceria	1.0 wt%	1		
Commercial ceria	1.0 wt%	1		
OCV hold test conditions	Type	Flow	RH	Pressure
94 h OCV hold anode fuel	H <sub>2</sub>	200 cm <sup>3</sup> min <sup>-1</sup>	30%	Ambient
94 h OCV hold cathode fuel	Air	200 cm <sup>3</sup> min <sup>-1</sup>	30%	Ambient
500 h OCV hold anode fuel	H <sub>2</sub>	350 cm <sup>3</sup> min <sup>-1</sup>	30%	150 kPa
500 h OCV hold cathode fuel	Air	830 cm <sup>3</sup> min <sup>-1</sup>	30%	150 kPa

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