Supporting Information

Fluoroalkyl Phosphonic Acid Radical Scavengers for Proton Exchange Membrane Fuel Cells

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Materials and methods

Materials

Nafion**™** D2020 was purchased from Ion Power. 1H,1H,2H,2H-Perfluorooctanephosphonic acid (PFOPA) and cerium nitrate hexahydrate was received from Sigma Aldrich. ePTFE membrane was received from Donaldson. The thickness of the ePTFE used for casting the membranes is 7 μm. Perfluorinated phosphonic acids (C6, C8, and C10) were synthesized following the procedure reported in our previous literature [1]

Membrane casting

2 gm of D2020 was taken and 2 ml of IPA was added to it. For making the phosphonic acid membranes, small molecules C8, C10, PFOPA in the calculated amount equivalent of 30 mol% of sulfonic acid in the Nafion was added to the above dispersion. Cerium in the amount of 5 mol% was added to make Ce-Nafion membrane. The dispersion was let to stir for 1 hr and then sonicated for 15 min. Then 12μm membrane was coated on the glass slide using a rod coating machine. The membrane was left to dry. ePTFE was soaked in Ethanol for 30 min and then washed with water and dried. This ePTFE film was then spread on the casted membrane. Another coat of Nafion dispersion equivalent to 12μm thickness was then coated on to the ePTFE film. The membrane was left to anneal at 130°C for 24 hr. and then further hot pressed at 130°C for 5 min. before doing further measurements. The final membrane thickness ranged from 28μm-30μm.

Aqueous Fenton reagent test (FRT)

FRT is an ex-situ test wherein radicals are generated to attack the Nafion™ sites and thereby reduce the membrane weight over time. Fluoride anions emitted are used as a measure of the degradation of Nafion™. Fenton solution was prepared by mixing 10 ppm Fe^{2+} ions along with 3 wt.% of H_2O_2. The solution was changed every 24 hr. All Fenton solution samples were collected to evaluate their fluoride concentration later using Dionex Ion Chromatography (Thermo Scientific). The test was repeated with three different membranes and the averaged values are reported as the observed FER. Error bars show the maximum in the FER observed for each membrane.

Fluorescence dye test

The fluorescence measurements were carried out using Cary Eclipse fluorescence spectrophotometer. The stock solutions for Fenton reaction were prepared as follows: 0.05 mM Dye, 2 mM FeSO$_4$ in 2 mM H$_2$SO$_4$, and 1 mM H$_2$O$_2$. Radical scavenger in concentration 2 mM were added first to the solution containing 0.5 ml Dye, 1 mL FeSO$_4$ sol., 1 mL of H$_2$O$_2$. The test solution was then mixed thoroughly, and

the dye intensity let to stabilize for 2 min. before taking the measurements.

Hydrogen pump migration testing

Membranes were cut into 1×3 cm^2 pieces. The line scan of the membrane was recorded using ORBIS X-Ray Fluorescence with a spot size of 30 μm, a 35 μm nickel filter, an accelerating voltage of 30 kV, and a tube current of 700 μA. All XRF analysis was based on the relative intensity of fluoresced Ce L-lines, which are the most prominent fluorescent Xrays emitted by Ce and arise at energy levels of 4.8 keV. The membrane was also scanned with Energy Dispersive X-Ray Spectroscopy (EDAX) at the beginning of the test. The membrane was then assembled into the BekkTech cell from Scribner. The cell was filled with hydrogen. The temperature of the cell was kept at 80°C and the hydrogen was pumped to the cell at 100% RH conditions. 0.4 V of potential was then applied to the membrane and the test stopped when 2C of charge was transferred across the membrane. Nitrogen was flushed through the cell to dry the membrane and the cell disassembled after it came down to the room temperature. The membrane was then tested under XRF and EDAX to measure the final counts across the length of the membrane.

Proton conductivity

Proton conductivity was extracted from the charge vs. time response of the various membranes in the hydrogen pump experiment using the formula V=IR. Where I = C/t, C is coulomb charge transferred and t is time in seconds. V is fixed at 0.4V. Conductivity was then calculated from σ (S∕m)=0.0425/(RWt), where R is the resistance in Ω, W is the width of the membrane in m and t is the thickness in m. 0.0425m is the distance between the working and the counter electrode.

Proton conductivity was measured by running the linear sweep voltammetry on the cell assembled for hydrogen pump experiment.

Mechanical property measurement

Mechanical properties of the membranes was measured using DMA Q800 from TA instruments. Membranes were cut into 0.6 cm * 2.5 cm pieces. The temperature of the chamber was maintained at 30°C and the humidity was kept at ambient humidity conditions. The piece was clamped in the chamber and then tensile stress was applied on the membrane at a constant rate of 0.5MPa/min till the membrane yielded.

Fuel Cell Performance

As-synthesized catalysts were incorporated into the MEA by directly spraying a water/n-propanol based ink onto a Nafion^{TM}211 membrane. An MEA of 5 cm^2 size was prepared with a Pt loading of ~ 0.1 mgPt/cm^2

on both anode and cathode for fuel cell testing. The MEA was sandwiched between two graphite plates with 14 straight parallel flow channels. The differential cell was operated at 80°C with 150 kPa absolute H_2/air at a gas flowrate of 1000/3000 sccm. Seven conditioning cycles were run before recording the performance and the CV for the various membranes. HFR was measured by doing EIS measurement in H_2/air and the value at 100kHz is reported. ECSA was obtained by calculating underpotentially-deposited hydrogen (HUPD) charge in CV curves between 0.1-0.4 V (0.4-0.45 V background subtracted) assuming a value of 210 µC/cm^2 for the adsorption of a hydrogen monolayer on Pt (CV curves were obtained under 150 kPaa H_2/N_2, 30°C, > 100 % RH, 1000/3000 sccm). MA was calculated by measuring the current density at 0.9V after 15 min hold and correcting the obtained current density for hydrogen crossover and HFR. Tafel slope was calculated from the polarization curve under H_2/air at a gas flowrate of 1000/3000 sccm by measuring the slope in the region of 0.7V to 0.9V.

Membrane durability testing

As-synthesized catalysts were incorporated into the MEA by directly spraying a water/n-propanol based ink onto a GDL obtained from SGL technologies. An MEA of 5 cm^2 size was prepared with a Pt loading of ~ 0.1 mgPt cm^2 on both anode and cathode for fuel cell testing. The fuel cell was operated at 90°C at 30%RH with 150 kPa H_2/air at a gas flowrate of 500/1000 sccm. The cell was held at OCV throughout the test. Cyclic voltammograms were recorded after every 24 hr. by switching the cathode side to nitrogen. CV were run from 0.05 to 0.95 V and the current density at 0.4 V is used to estimate the hydrogen crossover through the membrane. Every 24 hr., the effluent water was collected for the anode and the cathode side to measure the fluoride release rate using Ion Chromatography. The differential cell testing protocol and the MEA preparation for the same can be found in our previous study[1].

DFT calculations

In this study, DFT calculations were carried out based on Vienna ab initio simulation package (VASP)[2]. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE)[3]exchange-correlation functional were applied to perform the electron-ion interactions[4]. The plane-wave cutoff energy was set to 500 eV for all the calculations. The total energy and maximum force converged to less than 1.0×10^{-6} eV and 0.05 eV A^{-1}, respectively. The cubic unit cell of 15Å × 15Å × 15Å was employed to avoid the interaction beyond the periodic boundary condition. All calculations were carried out using 2 × 2 × 2 of Monkhorst-Pack k-point grids. To describing for the radical mechanism of phosphonic acid, the climbing image (CI) nudged elastic band (NEB)[5] as implemented in VASP.
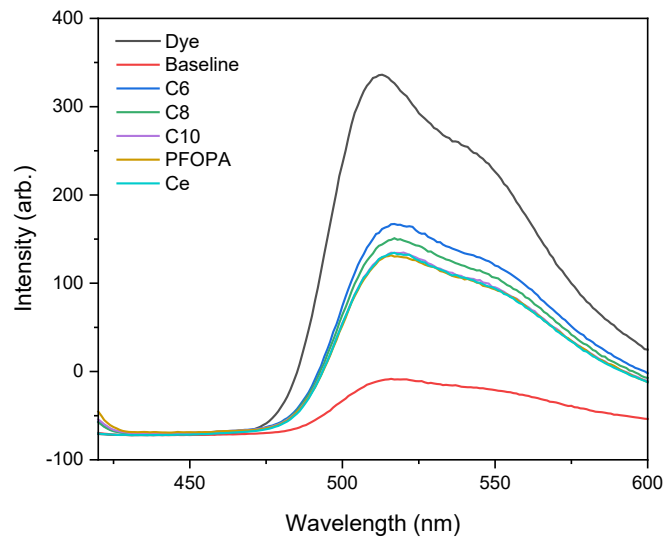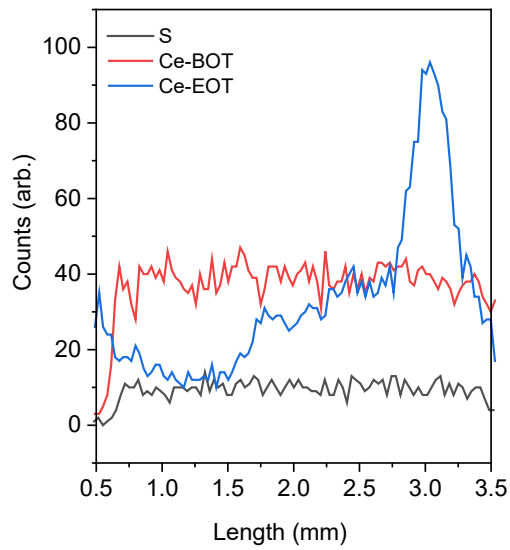
**Fig S1:** Intensity of 6-carboxyfluorescein with and without various radical scavengers
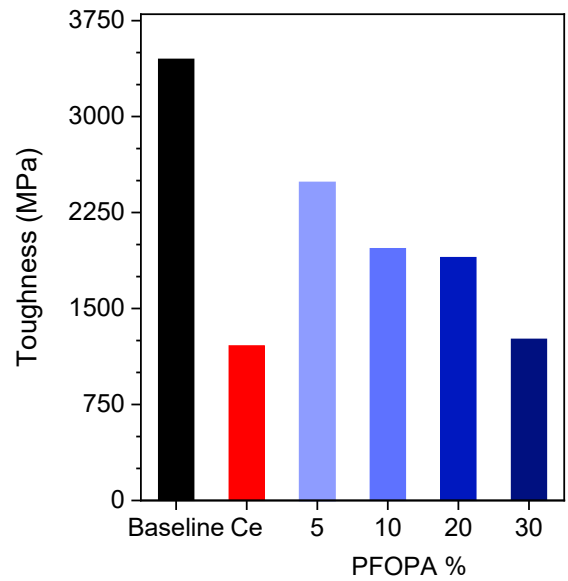
Fig S2: Tensile toughness of Ce-Nafion™ and PFOPA-Nafion™ as a function of PFOPA content.
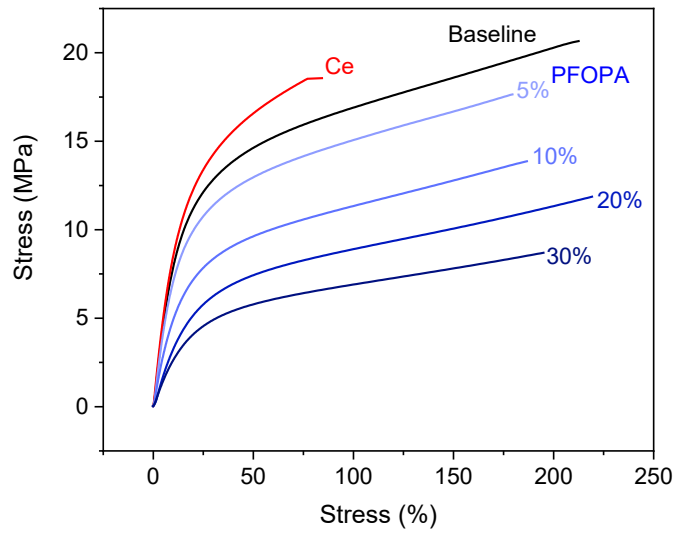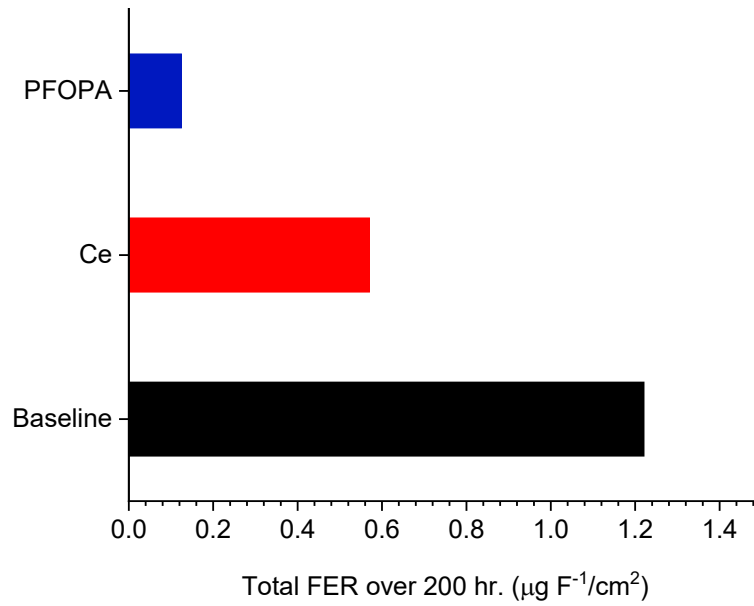
Fig S3: Stress-strain curves of PFOPA-Nafion™ as a function of PFOPA content.

Fig S4: XRF line scan for Ce-Nafion™ before and after the hydrogen pump migration test, S represents the counts of S from the Nafion side chain which remains unchanged before and after the test.
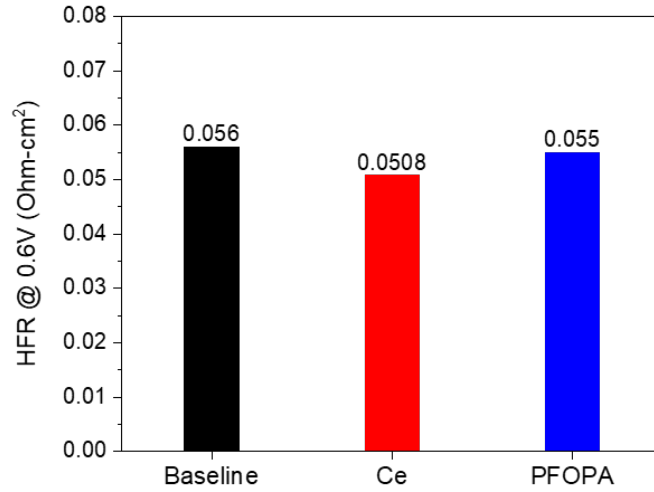
Fig S5: HFR comparison between the cell using Ce-Nafion™ and PFOPA-Nafion™.

Fig S6: Total Fluoride ions emitted over 200 hr. of OCV hold test for various membranes

References

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