Chemical degradation of fluorosulfonamide fuel cell membrane polymer model compounds

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HIGHLIGHTS

- Aromatic trifluoromethyl sulfonamide model compounds were prepared and degraded.
- Mono-, di- and tri-substituted compounds were compared.
- The mono-substituted compound shows greater stability than the di-substituted species.
- Loss of perfluorinated sulfonamide side chains is an important pathway.
- Dimerization and aromatic ring hydroxylation are also degradation pathways.

ARTICLE INFO

ABSTRACT

The durability of a polymer electrolyte fuel cell membrane, along with high proton conductivity and mechanical performance is critical to the success of these energy conversion devices. Extending our work in perfluorinated membrane stability, aromatic trifluoromethyl sulfonamide model compounds were prepared, and their oxidative degradation was examined. The chemical structures for the models were based on mono-, di- and tri-perfluorinated sulfonamide modified phenyl rings. Durability of the model compounds was evaluated by exposure to hydroxyl radicals generated using Fenton reagent and UV irradiation of hydrogen peroxide. LC–MS results for the mono-substituted model compound indicate greater stability to radical oxidation than the di-substituted species; loss of perfluorinated fonamide side chains appears to be an important pathway, along with dimerization and aromatic ring hydroxylation. The tri-substituted model compound also shows loss of side chains, with the mono-substituted compound being a major oxidation product, along with a limited amount of hydroxylation and dimerization of the starting material.

1. Introduction

Polymer electrolyte membrane (PEM) fuel cells have attracted significant attention as an alternative energy source that can deliver clean, secure and economic power in both stationary and transportation applications [1–5]. The polymer membrane is at the heart of a PEM fuel cell; it allows the transportation of protons, separates fuel from oxidant and maintains separation of the cathode and the anode layers; membrane failure therefore equates to cell death. Durability remains a major target for improvement in fuel cell systems, with numerous factors existent that can drive fuel cells through chemical, thermal and mechanical failure modes

[4,6–9]. A significant amount of research has been carried out in an effort to understand and address the design of novel membrane polymers, improving operation lifetimes, increasing conductivity of the membrane, advancing mechanical and thermal durability, and incorporating inorganic additives [10–13].

It is widely believed that hydrogen peroxide is generated and diffuses throughout operating fuel cells, with a commonly proposed mechanism postulated based on the reaction of hydrogen and adsorbed oxygen on the cathode [14]. Oxygen crossover from the cathode to the anode in the presence corrosion metal ions is also a potential sources of hydroxyl and hydroperoxyl radicals that can oxidize and destroy the membrane [15]. Simulation of hydrogen peroxide-based radical formation can be achieved using Fenton's reagent or UV/H_2O_2 degradation tests. The oxidation–reduction cyclic reaction of Fe(II)/Fe(III) in the Fenton test causes the formation of hydroxyl and hydroperoxyl radicals

continuously [16]. The effectiveness of H_2O_2/UV, which produces 2 mol of radicals per mole of photolyzed hydrogen peroxide, has been demonstrated as well [17]. In addition to resistance against chemical and mechanical degradation, fuel cell membranes must exhibit relatively high proton conductivity, high selectivity to proton permeability, high electrical resistance, especially at elevated temperatures [18,19]. Recent studies have shown that perfluorosulfonamide polymers have potential for use in PEMFCs, exhibiting favorable mechanical and chemical properties at elevated temperatures, coupled with high proton conductivity [19–23]. Such materials possess $-CF_3$ and $-SO_2$ groups, which have strong electron withdrawing effects, leading to high acidity and facilitated proton conduction. Fluorocarbon moieties are generally considered to be oxidatively stable, because of their strong carbon–fluorine bonds [24].

In the present work, the chemical stability and degradation mechanisms of synthetic model compounds (Fig. 1) which mimic perfluorosulfonamide polymers, in the presence of hydroxyl radicals, will be examined. Because placing multiple trifluoromethyl sulfonamide chains on single aromatic rings within PEM polymers is of potential interest as a means of enhancing proton conductivity, the mono-, di-, and tri-substituted model compounds will be examined.

2. Experimental

Aromatic trifluoromethysulfonamide ionomers, Fig. 1, were synthesized according to the method given below. M-SAMC refers to the mono-sulfonamide model compound; D-SAMC and T-SAMC refer to the di- and tri-sulfonamide model compounds respectively.

2.1. Preparation and characterizations of the ionomers model compounds

2.1.1. Materials

Benzenesulfonyl chloride, benzene-1,3-disulfonyl chloride, benzene-1,3,5-trisulfonyl chloride and trifluoromethanesulfonamide (Aldrich); ferrous sulfate heptahydrate (99%), hydrogen peroxide solution (H_2O_2, 30% w/v) and LC–MS solvents (acetonitrile, DI water, formic acid, trifluoroacetic acid – all HPLC grade) (Fisher Scientific) were all used as received.
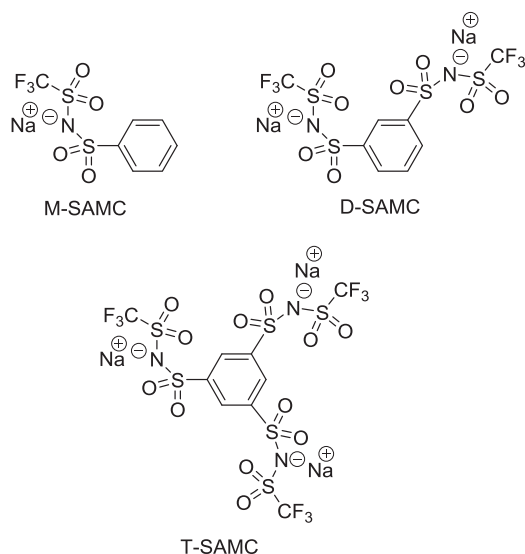

M-SAMC   D-SAMC

T-SAMC

Fig. 1. Chemical structures of sulfonamide model compounds.

Triethylamine (Aldrich) was dried over potassium hydroxide and freshly distilled.

2.2. Characterization techniques

2.2.1. Nuclear magnetic spectroscopy

^1H NMR and ^{19}F NMR were obtained at 600 MHz on Varian Inova Spectrometer VNMRJ 1.1D, software equipped with a Nalorac BB probe, at ambient temperature, dissolved in D_2O solvent, and internally referenced to TMS.

2.2.2. Liquid chromatography mass spectrometry

Mass spectra were recorded on Thermo-LCF10166 LC–MS system, which is equipped with an HP/Agilent Zorbax column (Allure biphenyl column 50 × 2.1 mm, 5 μm particles size). Samples were injected onto the column using flow rate 100 μl min^{-1}. The mobile phase used for gradient elution was acetonitrile/water containing 0.1% ammonium acetate. The solvent gradient started with (15:85 v/v) of water: acetonitrile for 2 min, then (30:70 v/v) of water: acetonitrile for 8 min. The column oven was maintained at 60 °C. Ionization of analysts was performed using electrospray ionization (ESI) in the negative mode, focused on 100–1000 m/z. A capillary temperature of 257 °C was employed. Retention time (RT) and mass spectral details are reported herein.

2.2.3. Synthesis and characterization of the model compounds

In a typical reaction, a solution of 0.35 g (2 mmol) benzenesulfonyl chloride in 2 ml anhydrous acetonitrile was slowly added to a cold (ice bath) solution of 0.3 g (2 mmol) trifluoromethanesulfonamide and 0.5 g (5 mmol) triethylamine in anhydrous acetonitrile. The reaction mixture was stirred for 2 h and allowed to warm up to room temperature and stirred for another 16 h. The mixture was washed with water and the product was extracted with chloroform. The organic layer was passed through an ion exchange membrane to obtain the product in the form of its sodium salt (95% yield), characterized by ^1H and ^{19}F NMR, and LC–MS.

N-[(Trifluoromethyl)sulfonyl]benzenesulfonamide; M-SAMC m.p. 56 °C; ^1H NMR (600 MHz, D_2O) δ 7.3 (s, 2H, aromatic), δ 7.4 (m, 2H, aromatic), δ 7.9 (s, 1H, aromatic). ^{19}F NMR (600 MHz, D_2O) δ −79.06 (3F, s). Mass (LCMS): m/z 288 (M^+ − Na). N,N′-bis[(trifluoromethyl) sulfonyl]benzene-1,3-disulfonamide; D-SAMC m.p. 170 °C; ^1H NMR (600 MHz, D_2O) δ 7.6 (m, 1H, aromatic), δ 8.0 (s, 2H, aromatic), δ 8.3 (s, 1H, aromatic). ^{19}F NMR (600 MHz, D_2O) δ −78.5 (3F, s). Mass (LCMS): m/z 499 (M^+ − Na). N,N′,N″-tris[(trifluoromethyl)sulfonyl] benzene-1,3,5-trisulfonamide;T-SAMC m.p. >250 °C; ^1H NMR (600 MHz, D_2O) δ 8.3 (s, 3H, aromatic). ^{19}F NMR (600 MHz, D_2O) δ −79.11 (3F, s) Mass (LCMS): m/z 755 (M^+ − Na).

2.3. Chemical degradation processes

2.3.1. Degradation using Fenton's reagent

Fenton Reagent degradation was carried out by treating 10 mM solutions of the model compounds with 1.25 mM of ferrous sulfate. The mixture was purged using nitrogen gas for 10 min to avoid radical quenching that may occur in the presence of dissolved oxygen. 11 mM of H_2O_2 was slowly added drop wise to accelerate the degradation reaction. The reaction solution was heated to 70 ± 2 °C and purged by nitrogen gas for 24 h. Another equal aliquot of ferrous sulfate was added to the mixture after 7 h. Approximately, 0.5 ml of the solution was taken after 1, 3, 5, 7 and 24 h to analyze for degradation using LC–MS.