

Chemical degradation of Nafion™ membranes

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Introduction

Fuel cell technology has emerged as a promising platform from which to deliver future energy needs¹. In the case of hydrogen fuel cells, the generated flow of electrons must be matched by flow of protons; this proton “conductance” typically occurs through a polymer membrane. Amongst the many ion conductive polymers, Nafion™ is a leading candidate because of its high ionic conductivity, high mechanical, thermal and chemical stability. While the physical properties, chemical stability, and the properties of Nafion-assembled fuel cell systems are widely discussed in the literature, conclusions on the durability of Nafion used under fuel cell operating conditions are confusing and sometimes contradictory. A systematic investigation of the durability of Nafion under fuel cell operating conditions, and chemical changes in the polymer which may result during this operation is necessary. Our efforts focus on chemical changes in Nafion and in low molecular model compounds chosen to probe potential sites of chemical degradation within the membrane polymer. In this preliminary report of Nafion durability under accelerated lifetime conditions, a systematic study of chemical decomposition products resulting from Nafion decomposition in the presence of peroxide/hydroperoxide radicals is presented. Similarities between fluoropolymer decomposition and that of small molecule analogs are discussed with an eye towards mechanistic explanation of Nafion decomposition, and design of more robust proton conduction membranes. Experimental details which can lead to erroneous measurements during such aging studies will also be presented as part of a large family of control experiments. The dynamics of ferrous/ferric ions during Fenton’s aging experiments will also be explained in detail in this work. In addition to this report of changes in Nafion as a result of accelerated lifetime testing, similar results will be presented in which small fluorochemical molecules approximate the different functionalities within Nafion.

Experimental

Equivalent weight (EW) of the Nafion ionomer determined by acid-base titration, is directly related to the concentration of pendant sulfonate groups within the polymer, and can be used as an indirect measurement of potential ion conductivity. Nafion (fresh/aged) films in their protonated form (H⁺) were dried in vacuum oven (c.a. 100°C) for 1-2 hours, weighed, soaked in 3M aqueous NaCl overnight to exchange Na⁺ for H⁺, and were finally titrated with 1-3 mM aqueous NaOH to an end point as indicated using a pH meter (Mettler-Toledo) and a phenolphthalein color change. The EW was determined as the weight of dry polymer in grams/mol

of exchange sites of the sulfonic acid groups. Aging experiments were carried out using Fenton’s reagent²; the mechanism of the resulting radical generation using this treatment is shown in Figure 1. The Nafion film samples were immersed in a flask containing the Fenton’s reagents (Fe²⁺, c.a. 80mM; H₂O₂, c.a. 400mM; Nafion film, c.a. 0.5g) as discussed above, and during the course of aging experiment 3 additional follow-up additions of H₂O₂ were added in the flask to maintain the concentration of radical-generating species. The system was continuously bubbled with argon and maintained to be 70°C, which closely approximates polymer fuel cell operating temperatures. The concentration of fluoride ions was measured by an ion selective electrode (ISE) (Mettler-Toledo), which was calibrated over the range 0.01 – 1000 ppm fluoride using NaF aqueous solutions.

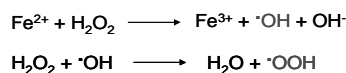


Figure 1. Fenton’s reactions to create radicals (pH < 3).

Results and Discussion

From Figure 2, fluoride ion generation is indeed observed during Fenton’s Reagent aging of Nafion membrane. This result is different from control experiments in which Nafion film is exposed only to deionized water, and no detectable fluoride is generated

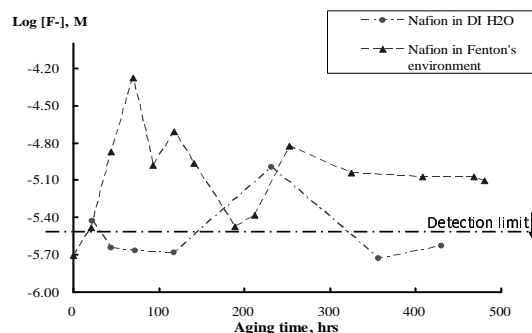


Figure 2. F⁻ concentration of the system as a function of aging time.

EW changes as a function of aging time as shown in Table 1. The EWs of the fresh and aged samples are found to hardly change. However, combined with the Fenton’s aging experiment settings and fluoride release data, one can conclude that the H₂O₂ added might decompose and react quickly which in turn exhausts the available supply of ferrous ions. Should this be the case, further generation of radicals would be hindered, and Nafion decomposition would be limited.

Table 1. EW Comparison of Nafion and Aged samples

Sample	EW
Nafion fresh	1115 ± 50
Nafion aged	1132 ± 20

References

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