A statistical mechanical approach to model main chain scission in PFSA ionomer membranes

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Radical attack is known to be the main cause of the chemical degradation in perfluorosulfonic acid (PFSA) ionomer membranes of polymer electrolyte fuel cells [1-2]. The attack can result in chain scissions [2] that have been quantified experimentally by fluorine release [3] and number average molecular weight measurements [4].

Chain scission is a random process that induces the structural changes and degradation in ionomer and its properties, respectively. In this study, a statistical mechanical approach is applied to model this random process to provide a full picture of the evolution in molecular weight distribution rather than the average molecular weight.

One of the current understandings of PFSA ionomer membrane chemical degradation is shown in Fig. 1. Chemical degradations are assumed to be initiated by the side chain cleavage followed by an unzipping mechanism that further causes the chain scission at main chain [2-4]. Each scission breaks the main chain into two fragments, and the total concentration of all fragments, $C_t = \int_0^\infty c(x,t)dx$, can be described by the rate equation written in the following:

$$\frac{dC_t}{dt} = kc_{\mathrm{OH}\cdot}\, c_{\mathrm{O}\cdot} = r \qquad [1]$$

which is solved in a one-dimensional numerical membrane electrolyte assembly (MEA) model that is developed to simulate transport phenomena of ionomer phase species, including OH· radical and -O· intermediate radical (Fig. 1), and gas phase species (*e.g.* oxygen and hydrogen) under various fuel cell operating conditions. In order to model the evolution of the individual concentration of x-mers, $c(x,t)$, at time t, the kinetic equation that describes binary chain scission is applied [6-8]:

$$\frac{\partial c(x,t)}{\partial t} = -c(x,t)\int_0^x F(y,x-y)dy + 2\int_x^\infty c(y,t)F(x,y-x)dy \qquad [2]$$

in which $F(x,y)$ represents the rate of breaking $x+y$-mers into two smaller fragments, x-mers and y-mers. Assuming that all chain scissions are random, the intrinsic rate, F, reduces to a constant. Its value can be calculated through the following relations that are derived from Eq. (2):

$$\frac{d}{dt}\int_0^\infty c(x,t)dx = \frac{FM}{M_{\mathrm{mon}}} = r \qquad [3]$$

where

$$\frac{M}{M_{\mathrm{mon}}} = \int_0^\infty yc(y,t=0)\,dy. \qquad [4]$$

The total mass of all fragments (per volume), M, is a product of the average molar mass of main chain per sulfonic acid group and the sulfonic acid group concentration of dry PFSA ionomer membrane at the beginning of life, and M_{mon} is the molar mass of one monomer. Finally, the molecular weight distribution is:

$$n(x,t) = \frac{c(x,t)}{C_t} \qquad [5]$$

where

$$c(x,t) = e^{-Ftx}\left(c(x,0) + \int_x^\infty c(y,0)[2Ft + F^2t^2(y-x)]dy\right) \qquad [6]$$

is the solution of Eq. (2). The distribution will be applied to evaluate membrane characteristics, *e.g.*, the ion exchange capacity and the fluoride release rate, during chemical degradation under various fuel cell operating conditions, including accelerated stress test (AST) condition [4].

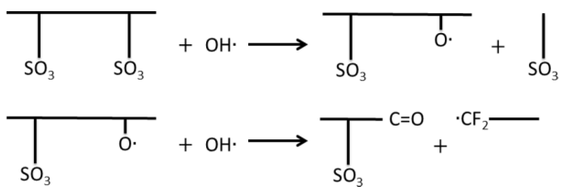

Fig. 1: Schematic of the side chain degradation considered in the present study: side chain cleavage (top) and main chain scission (bottom).

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