

Physico-chemical modeling of degradation phenomena in polymer electrolyte membranes

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Polymer electrolyte fuel cells (PEFCs) are intensively studied as promising power sources for automotive as well as stationary applications. Perfluorinated sulfonic acid (PFSA) ionomer membranes fulfill most of the performance requirements for use in fuel cells. However, chemical ionomer degradation remains a major concern. Profound understanding of the chemical degradation mechanisms of PFSA ionomer membranes is of paramount importance in the development of robust and efficient PEFC technology. It is generally assumed that the chemical degradation of PFSA ionomer membranes is caused by the attack of free radicals, such as hydroxyl ($\bullet\text{OH}$) radicals, to vulnerable chemical groups of ionomer backbone and side chains. In this work, we develop and evaluate a comprehensive kinetic model to account for the major pathways of radical formation and radical attack on ionomer molecules. In the first step, we formulate and systematically simplify a set of equations that accounts for the currently known mechanisms of radical formation and consumption under *in situ* (fuel cell) and *ex situ* (Fenton test) conditions in PEM. The model provides radical concentrations as a function of initial iron content and hydrogen peroxide (H_2O_2) concentration. In the second step, time-dependent radical concentrations are used to describe pertinent degradation mechanisms based on the attack of $\bullet\text{OH}$ to sulfonate head group and ether group in the ionomer side chain. Comparison with extensive experimental reports in the literature is used to parameterize and simplify the model [1-7]. For evaluation purposes, we compare model results with experimental data such as fluoride emission rate, NMR data, carboxylic acid group (COOH) concentration, and changes in ion content. Thereby, the model provides fingerprints for the distinction of degradation pathways.

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