

Mechanism of Hydroxyl Radical Attack on PFSA  
Ionomer: A Solid State Q-NMR Study  
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The chemical structure of Nafion<sup>®</sup> 211 was monitored using calibrated <sup>19</sup>F magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy upon exposure to hydroxyl radicals. Fluorine loss in each individual segment of the ionomer was calculated and compared as a function of reaction time with OH radical.

The data reveals that the main chain of Nafion<sup>®</sup> 211 is not the starting point for the OH radical attack and is resistant to Fenton's reagent up to 48h. In this situation the degradation occurs solely on the side chain, with the most significant attack occurring toward the end of the side chain. The quantitative <sup>19</sup>F MAS NMR data also explains why that the proposed mechanism for chemical degradation of the side chain has a similar rate of fluorine loss in the  $\alpha$ -OCF<sub>2</sub> unit (the ether group closer to the end of the side chain) and the SCF<sub>2</sub> group. Based on these results, the  $\alpha$ -OCF<sub>2</sub> group is believed to be the first point of attack by oxygenated radicals.

The technique is proven reliable and accurate and can be used for comparing the durability of all forms of PFSA ionomers, including shorter side chain ionomers such as Aquivion<sup>®</sup> and 3M<sup>®</sup> membranes.